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RAY T. BAYLESS, *Editor*

Vol. XXII April, 1934 No. 4

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MICROSCOPIC CRACKS IN HARDENED STEEL, THEIR EFFECTS AND ELIMINATION

By E. S. Davenport, E. L. Roff and E. C. Bain

Abstract

The studies described in this paper are the outgrowth of the authors' earlier work on the rates of transformation in steel. In measuring the transformation velocity of steels at various constant temperatures it became apparent that the products of transformation at temperatures hitherto unused were unique and might possess unusual properties. The influence of grain-size upon transformation rate had likewise been investigated and the grain-size study is here extended to include its effect upon the properties of steel, both as quenched and tempered in the usual manner, and as hardened at a constant elevated temperature.

This paper sets forth observations which support the following interpretations:

1. The brittleness of fully-hardened and tempered steel is due, in part at least, to the presence of real or potential microscopic quenching cracks. The micro-cracks, or their causes, may not be wholly removed in tempering, once they are developed in the martensite. In one instance a heating to 2000 degrees Fahr. (1090 degrees Cent.) was required to eliminate them.

2. Steel treated to secure a moderately high hardness, e.g., Rockwell C 50, by means of a direct austenite transformation at a constant temperature appears to be free from micro-cracks, and is very much tougher than the conventionally quenched and tempered steel of identical hardness, although heated to the same quenching temperature and having the same austenitic grain-size.

3. The prevalence of the micro-cracks increases with the austenitic grain-size; severe loss of impact resistance accompanies increase in grain-size. Increased grain-size affects adversely even the crack-free steel, although to a much slighter extent.

4. Fine grain-size greatly improves the toughness of hard, quenched and tempered steel and the value of alloy steel may reside largely in the ability of the alloying ele-

The authors, who are members of the Society, are associated with the Research Laboratory of the U. S. Steel Corporation at Kearny, N. J. Manuscript received January 19, 1934.

ments to provide sufficient hardening capacity to counteract the low hardenability contributed by an extremely fine grain-size. The fine grain-size may be secured by the presence of the deep-hardening element itself, by other elements, or by the deoxidation technique in steel making which is believed to introduce a fine dispersion of non-metallic particles capable of inhibiting grain-growth.

Introduction

IN the heat treating of carbon steels, selected and quenched to develop full martensitic hardness, it is by no means uncommon to encounter cracking of the pieces immediately following the extremely rapid cooling resorted to in order to induce the desired hardness. The nature and location of the cracks, as well as the effective means of minimizing them, such as design free from sharp corners, tempering before the pieces reach even room temperature, etc., all persuade one to impute to fully hardened steel the presence of very high stresses. The demonstration of the existence (and a fair estimation of the intensity) of these balanced stresses when distributed in a general symmetrical manner has been accomplished by Heyn,[1] and by many others following his methods. From the rapidly accumulating knowledge on the crystal physics and the mechanism of formation of martensite (hardened steel), it may be reasoned that high stresses of a different distribution are likewise developed, i.e., stresses of microscopic distribution, balanced, tension against compression, perhaps within the space of an individual original austenite grain. Stresses substantially uniform over large zones in the shape may come into existence through thermal contraction alone in a rapidly-cooled object; the microscopic stresses, on the other hand, are believed to be the result of dimension changes within the crystal involved in the transformation of the austenite, occurring as it does in a step-wise manner, to form martensite. While the two types of stress may in the last analysis have something in common, it is convenient to regard them as genetically independent. This paper deals primarily with the stresses of minute distribution and the microscopic ruptures they induce.

As early as 1922 Rawdon and Epstein[2] showed photomicrographs of minute cracks in etched martensite, the essential constituent of

[1]Heyn-Grossmann, "Physical Metallography," John Wiley and Sons, 1925, p. 282-291.

[2]H. S. Rawdon and S. Epstein, "Structure of Martensitic Carbon Steels and Changes in the Microstructure which Occur upon Tempering," Scientific Papers, Bureau of Standards, 1925, Vol. 18, p. 373-409.

hardened steel. Lucas,[3] in his 1931 Howe Memorial Lecture, discussed these microscopic quenching cracks in detail and pointed out that they were evident, after etching, even when the steel had been tempered at 400 degrees Fahr. (200 degrees Cent.), a temperature sufficiently high to effect considerable change in the hardened steel. Lucas further suggested that such cracks, if present in a quenched and tempered steel, would undoubtedly greatly injure the fatigue resistance of the metal. With no further inquiry into the nature of these micro-cracks one would be justified in the assumption of very high balanced stresses in the martensite resulting from the transformation of an individual grain of austenite, for the cracks are very short in comparison with the average diameter of an austenite grain. Typical quenching cracks of this type are shown in the photomicrograph of Fig. 1. Although, as will be discussed, the minute ruptures under consideration are generally developed by etching, and might therefore have been designated as "etching cracks," it seems preferable to refer to them in this report as "micro-cracks" or "quenching cracks."

In this present paper some studies are reported which indicate a correlation between the occurrence of these quenching cracks and the ductility and impact strength of the steel in which they have been developed. It appears also that the severity of the micro-cracks is a function of the austenite grain-size of any given steel which is subject to this defect.

The Effect of Micro-cracks upon the Properties of Quenched Steel

If one is to recognize unequivocally the influence of the minute cracks, specimens must be studied and compared which differ only with respect to the cracks; composition, grain-size, heating temperature and final hardness should be identical. At first glance it may appear impossible to control the degree of cracking in specimens from the same bar of steel so similarly handled, and so far as is known at the present time, no such control can be exerted upon fully-hardened, wholly-martensitic specimens from the same steel bar. However, a method for preventing quenching cracks, even in the most susceptible steels, has been developed for products of

[3] F. F. Lucas (Howe Memorial Lecture), "On the Art of Metallography," *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1931, p. 11-44.

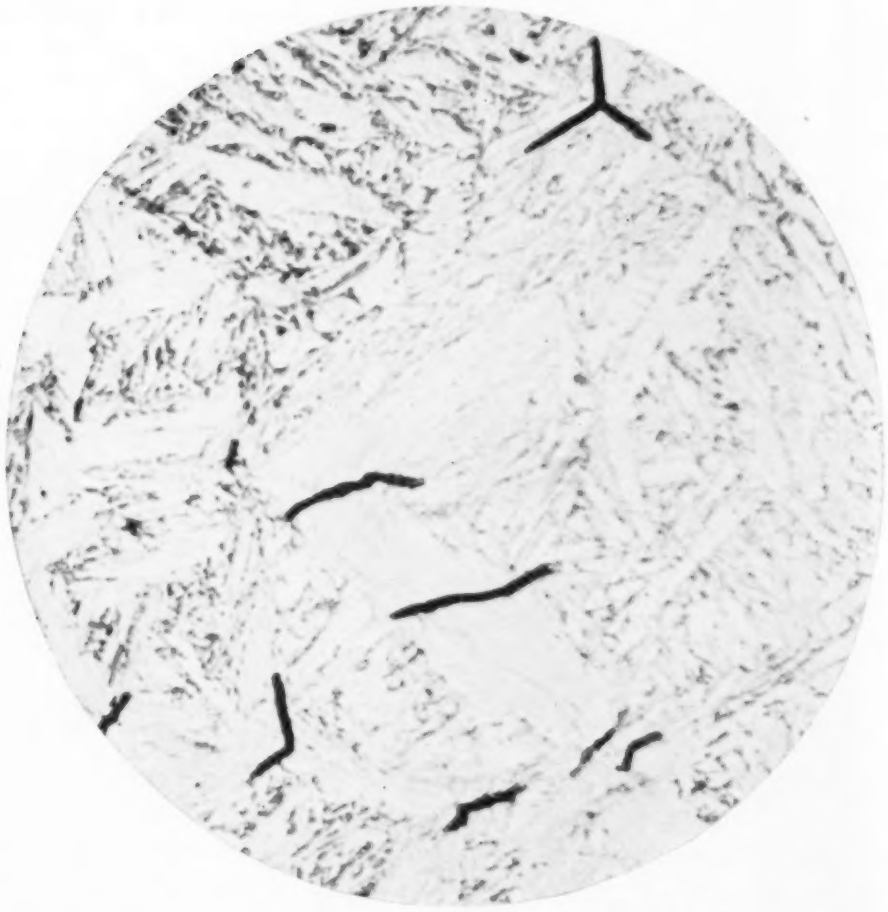

Fig. 1—Example of Typical Micro-Cracks in Martensite; 1.13 Per Cent Carbon Steel. × 2200.

a hardness value approaching, but not quite attaining, that of pure untempered martensite. With such specimens may be compared other specimens from the same steel which have been quenched conventionally to produce cracks and then tempered to match in hardness the crack-free specimens. Such a comparison seems certain to deal only with the influence of the factor under consideration, the influence of microscopic cracks. It should be recalled that Lucas[3] observed the cracks in tempered specimens, and further proofs will be offered here that the potentialities for cracks may be rather persistent.

Briefly, the new method[4] for treating steels to secure a hardness corresponding to that of only moderately-tempered quenched

[4]See U. S. Patent No. 1,924,099 covering this method of heat treating.

steel consists in allowing the steel to transform directly from the austenitic condition to the desired product without first passing through the intermediate state of hard martensite.[5] This is accomplished by quenching the properly heated, and therefore austenitic, steel directly into a bath of high heat-abstracting power which is itself maintained, however, at a chosen elevated temperature at which martensite is not produced. The steel must remain in this quenching bath for a time sufficient to permit substantially all the austenite to transform if a product essentially free from martensite is desired; otherwise, upon cooling to ordinary temperature, that part of the metal as yet untransformed will become martensitic.

The broad subject of the transformation of austenite at various constant subcritical temperatures has been investigated by the authors and reported in the publication to which reference is made. This inquiry focused attention upon the influence of transformation temperature upon both the velocity of reaction and upon the nature of the product of transformation. Indeed, the work reported in the present paper is essentially an outgrowth of the earlier investigation, for it early became apparent that the products of transformation at temperatures in the general range 250-900 degrees Fahr. (120-480 degrees Cent.) were hitherto hardly known and probably possessed unique properties.

The hardness of the products of direct austenite transformation at various constant temperatures is shown in Fig. 2 as observed in the case of several steels of the following compositions:[6]

	Carbon	Manganese	Silicon	Sulphur	Phosphorus	Chromium
A	1.13	0.30	0.171	0.015	0.026	....
B	0.78	0.36	0.160	0.048	0.036	....
C	0.54	0.46	0.198	0.041	0.048	....
D	0.50	0.91	0.131	0.041	0.046	....
E	0.64	1.13	0.094	0.030	0.048	....
F	1.17	0.30	0.180	0.033	0.026	0.26

The important feature of this method of treatment is that the products of direct austenite transformation at constant temperatures above about 400 degrees Fahr. (200 degrees Cent.) are free from the minute cracks described above. No definite temperatures can be specified here, for steels vary in this respect; the figure men-

[5] E. S. Davenport and E. C. Bain, "Transformation of Austenite at Constant Subcritical Temperatures," *Transactions*, American Institute of Mining and Metallurgical Engineers, Iron and Steel Division, 1930, p. 117.

[6] See Footnote 5.

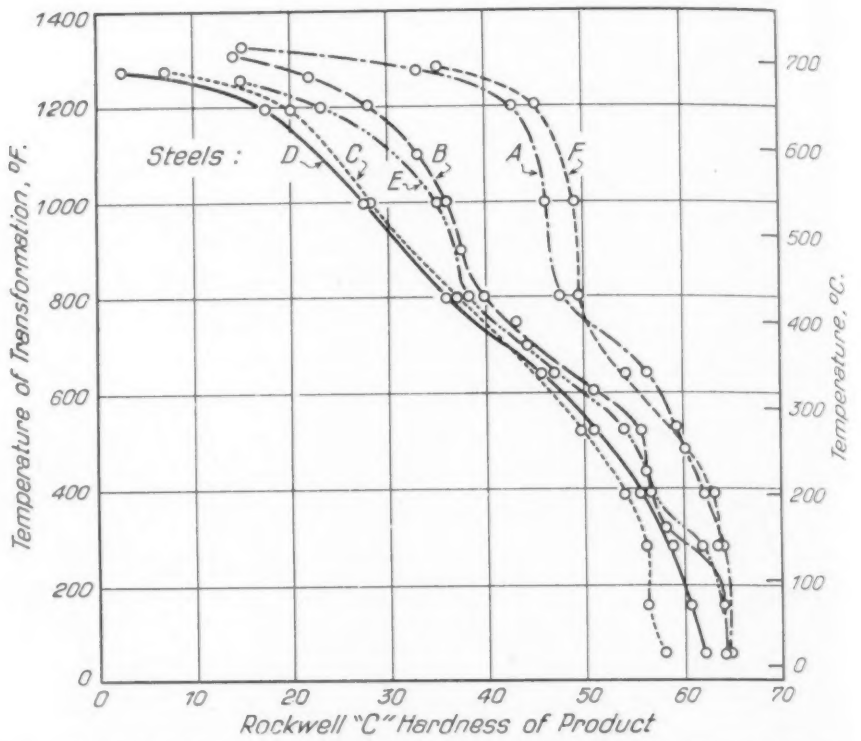

Fig. 2—Hardness of the Products Obtained from Complete, Direct, Austenite Transformation at Indicated Temperatures for Six Common Steels.

tioned refers, however, to the steels selected for discussion in this paper and to most similar steels. By the method outlined, specimens with the hardness of variously-tempered, quenched steels may then be produced free from cracks, suitable for comparison with specimens of the same steel carrying the cracks.

A few trials will quickly indicate a suitable time-temperature combination for tempering a brine-quenched specimen so as to match the hardness of the specimen from the new or direct transformation-from-austenite process. Either a short time at a higher temperature or a longer time at a lower temperature may be employed for the tempering, but in many cases the short time at the higher temperature yields the tougher product.[7] The chart of Fig. 3 shows the time-temperature combinations required for reducing the original quench hardness of 69 Rockwell C to 65, 60, 55, 50, and 45 Rockwell C in a typical steel of the following analysis:

C	Mn	Si	S	P
1.13	0.30	0.171	0.015	0.026

[7]The phenomenon of "temper brittleness" doubtlessly enters into the tempering process of many steels—presumably the ones employed here. To minimize this possibility the specimens were quenched into water from the tempering temperature.

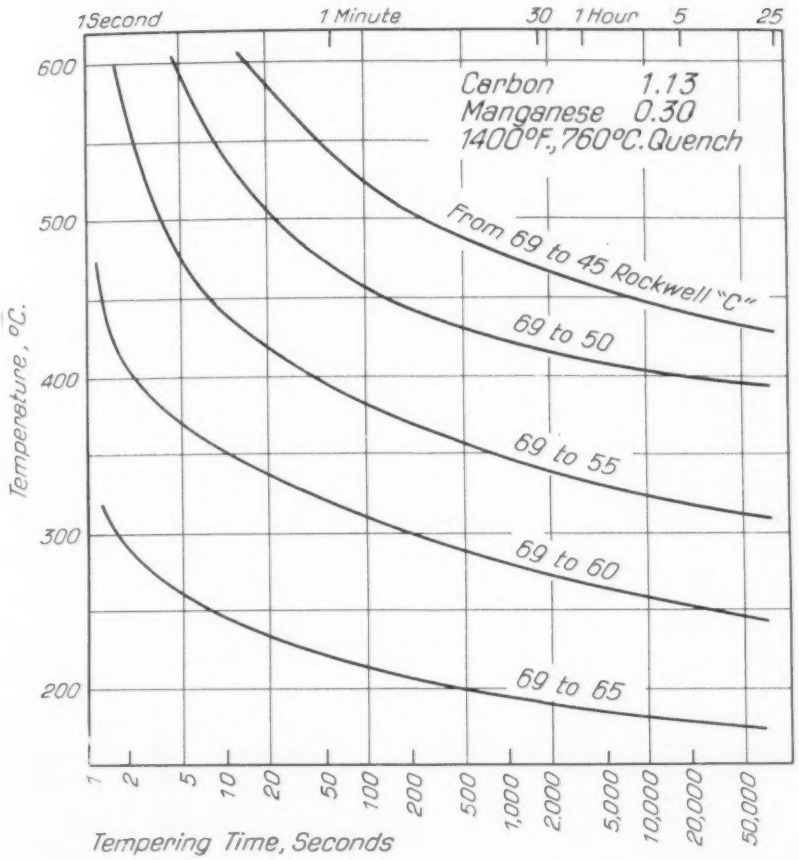

Fig. 3—Temperature and Time-Interval Combinations Required in Securing Several Specific Degrees of Softening by Tempering.

Very similar charts have been prepared for a variety of steels and the literature on the subject is abundant.

The photograph of Fig. 4 shows clearly the very great difference in physical characteristics of a typical steel of 0.74 per cent carbon, as set up by the two methods of treatment to secure a Rockwell hardness of C 50. The upper comparison is of tensile test specimens 0.180 inch in diameter. The middle comparison is of impacted specimens, unnotched Charpy test. The lower pair are slow bend specimens. Table I shows the heat treatments and the resultant mechanical properties for the two methods, that is to say, of specimens with and without cracks.

This single detailed comparison of samples of equal hardness, prepared, on the one hand to minimize the occurrence of microcracks, and on the other hand so as to develop them freely, is quite

Table 1
Treatments and Mechanical Properties

	C	Mn	Si	S	P
Analysis	0.74	0.37	0.145	0.039	0.044

New Method, Direct from Austenite, Crack-free	Quench and Temper Method, Containing Micro-cracks
Heat 5 minutes at 1450 degrees Fahr. (790 degrees Cent.)	Heat 5 minutes at 1450 degrees Fahr. (790 degrees Cent.)
Quench into lead-alloy bath at 580 degrees F. (305 degrees Cent.)	Quench into oil at 70 degrees Fahr. (21 degrees Cent.)
Let specimens remain in bath for 15 minutes	Temper immediately in lead-alloy bath 30 minutes at 600 degrees Fahr. (315 degrees Cent.)
Quench into water	Quench into water

Mechanical Properties (Average of 6 Tests)		Mechanical Properties (Average of 6 Tests)	
Rockwell C Hardness	50.4	Rockwell C Hardness	50.2
Ultimate Strength (lbs. per sq. in.) ..	282,700	Ultimate Strength (lbs. per sq. in.) ..	246,700
Yield Point (lbs. per sq. in.)	151,300	Yield Point (lbs. per sq. in.)	121,700
Elongation (per cent in 6 in.)	1.9	Elongation (per cent in 6 in.)	0.3
Reduction in Area (per cent)	34.5	Reduction in Area (per cent)	0.7
Impact* (Ft.-lbs.)	35.3	Impact* (Ft.-lbs.)	2.9

*Ft.-lbs. absorbed in breaking 0.180-inch round, unnotched specimens.

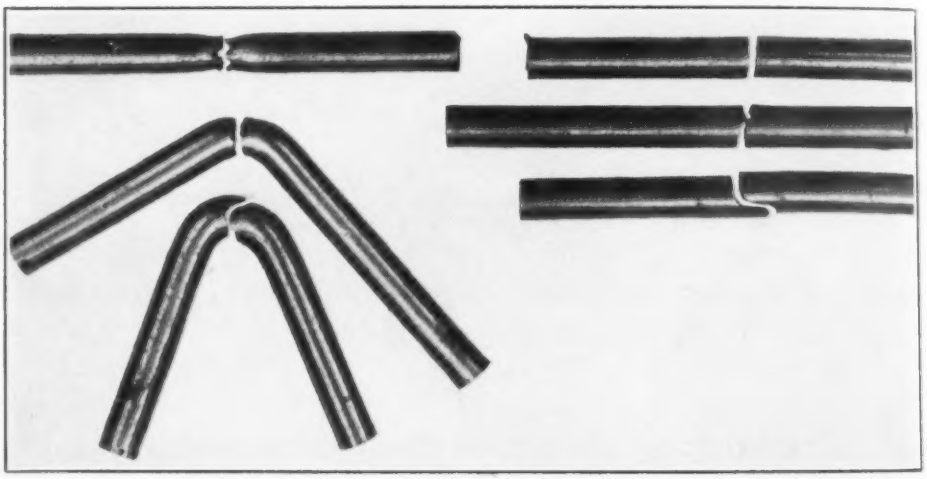

Fig. 4—Comparison of Test Specimens Prepared (Left) by Direct Transformation Method and (Right) by Usual Quench and Temper Method. Upper Pair, Tensile Specimens; Middle Pair, Impact Specimens; Lower Pair, Slow Bend Specimens. All 50 Rockwell C.

typical of all the comparisons. It has been observed that the difference in toughness and ductility distinguishing the two methods decreases as the hardness of the compared specimens approaches that of fully hardened steel, Rockwell C 60-65, and also as the hardness approaches the distinctly softened steel, about 40 Rockwell C hard-

ness. This is illustrated in the case of a steel which was studied at a variety of hardness levels and portrayed in Fig. 5. Here the impact values are plotted as a function of hardness and the wide disparity in toughness in the range about Rockwell C 50 is clearly evident.

The practical identity of the toughness achieved by the two methods in the high hardness range (Rockwell C 60 and above)

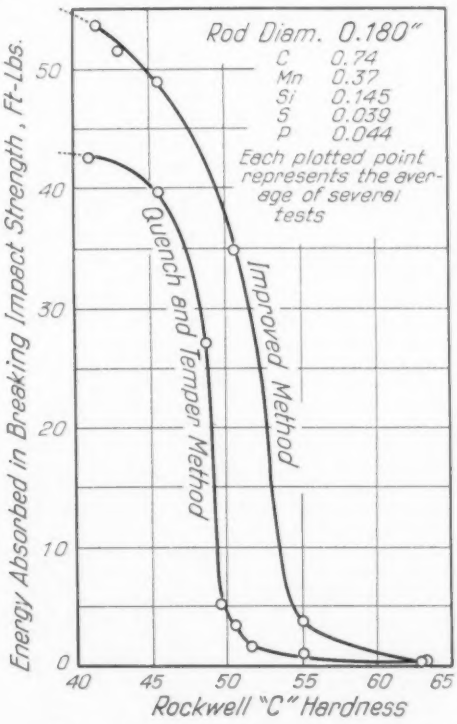

Fig. 5—A Comparison of the Impact Strength Obtained in a Steel Treated by the Two Indicated Methods to Secure Various Degrees of Hardness.

is to be expected since in securing this high hardness the difference in the methods practically vanishes because the transformation temperature for the new method is necessarily so low. In other words, the product, by either method, is very close to martensite and the constant temperature transformation bath becomes a martensitizing bath. (See Fig. 2.)

As for the apparently similar toughness at the lower hardness range, one might at this point suggest the following explanations:

1. The impact test itself becomes somewhat insensitive at high impact values.

2. The minute cracks heal during the high tempering treat-

ment. Serious doubt will be cast upon this hypothesis in subsequent paragraphs.

3. The cracks never really exist until after polishing and etching for examination under the microscope, and the high tempering treatment removes the stress concentrations necessary for opening them up during etching.

4. The cracks, when in the softer tempered material, have little effect upon its toughness.

An inquiry into the plausibility of these various possibilities will be found at the close of the paper. In the meantime it may be advisable to look further into the circumstances attending the development of the cracks with only the one assumption in mind—that reduced ductility is accompanied, if not caused, by the presence of the cracks, real or potential.

The Influence of Grain-size upon Microscopic Cracking and Toughness

The authors in previous studies leading up to the present one have observed the profound influence of austenitic grain-size upon the behavior of steel.[8] It may well be that grain-size, or possibly some still more fundamental condition responsible for the grain-growth tendency, is the most important single factor in determining the nature of a heat treated steel. It has been shown that an increase in the austenitic grain-size in a steel about to be quenched influences the hardenability of the steel much in the manner of added alloying elements which likewise tend to retard the transformation. A decrease in transformation rate is alone responsible for greater hardening capacity.[9] The significance of grain-size in the austenitic steel is so fundamental that two specimens of the same hypereutectoid steel, cooled at the same slow rate, may show a great disparity in "normality" if the one (normal) is composed of coarse austenite grains and the other (abnormal) of fine grains. A section of carbon steel which would, as ordinarily quenched, have a soft core of fine pearlite, may harden throughout if, prior to quenching, the grain has been coarsened by a brief heating at a still higher temperature than that required merely for austenite formation. The objection to this practice of quenching coarsened steel when applied to ordinary

[8] E. C. Bain (Campbell Memorial Lecture), "Factors Affecting the Inherent Hardenability of Steel," Transactions, American Society for Steel Treating, 1932, Vol. 20, p. 385-428.

[9] See Footnotes 5 and 8.

carbon steels is that gross cracking of the piece is likely to result. If such stresses are set up as to cause this visible rupture in such coarsened and hardened steel, one might reasonably expect to find some increase in the number and size of the microscopic cracks likewise brought about by the coarsening. This prediction appears to be correct on the basis of some observations on the influence of grain-size upon cracking and impact strength which are here offered.

In Fig. 6 is shown the effect of various measured austenitic grain-sizes upon the prevalence of microscopic cracks in the quenched,

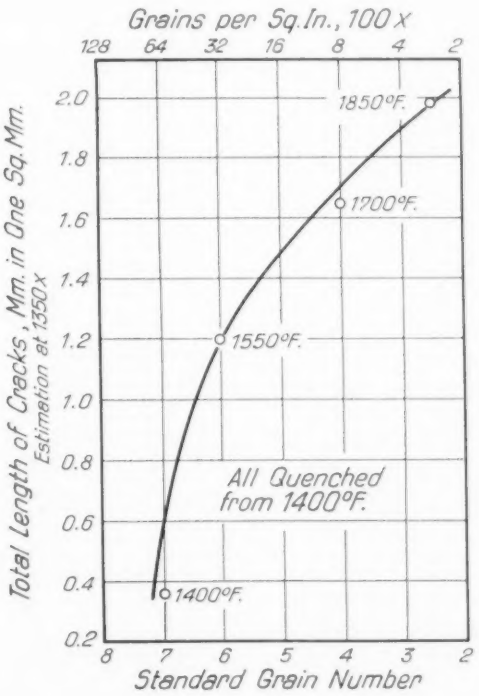
Grains per Sq.In., 100 X
128 64 32 16 8 4 2
Total Length of Cracks, Mm. in One Sq. Mm.
Estimation at 1350x
2.0 1.8 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2
1850°F.
1700°F.
1550°F.
All Quenched from 1400°F.
1400°F.
8 7 6 5 4 3 2
Standard Grain Number

Fig. 6—The Extent of Micro-Cracking in a Quenched Steel as Increased by the Coarsening of the Austenite Grain. Specimens Heated as Indicated but Quenched Thereafter from 1400 Degrees Fahr. (760 Degrees Cent.).

untempered steel. The evaluation of the severity of the cracking presents a difficulty which was satisfactorily overcome by measuring the total length (millimeters) of the traces of all the cracks in a given area (1 square millimeter) in the variously coarsened specimens. For this purpose much time and patience is required, for a nominal magnification of some 1000 to 1500 diameters and the utilization of the 90 × oil immersion objective with perhaps a 15 × eye-

piece seems unavoidable. Significant estimates of the prevalence of cracking also may be secured by merely counting cracks but this method penalizes the coarser grains which contain the longer cracks likely to be more serious contributors to brittleness. In Fig. 6 one may also read the heating temperature required to develop the grain-size indicated on the abscissa, but it should be noted that for each

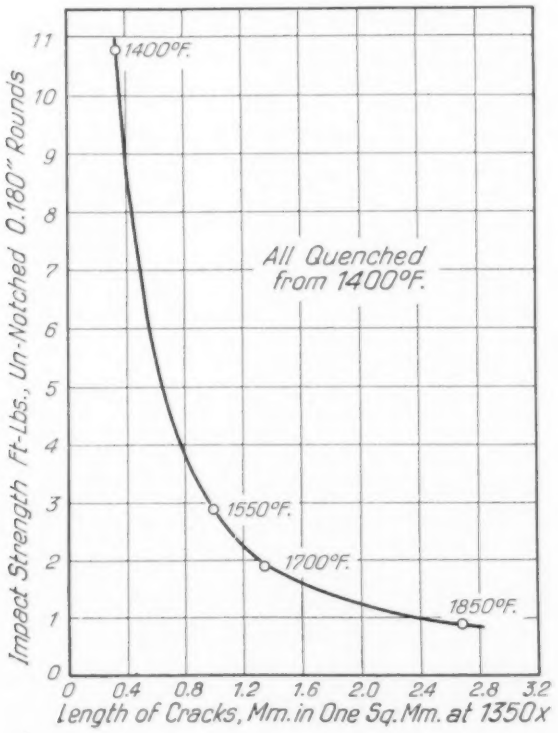

Fig. 7—Impact Strength of Quenched and Tempered (50 Rc) Steel Plotted as a Function of the Extent of Micro-Cracking. Specimens Heated as Indicated but All Quenched from 1400 Degrees Fahr. (760 Degrees Cent.); Tempered 30 Minutes at 700 Degrees Fahr. (370 Degrees Cent.).

specimen the quenching temperature was 1400 degrees Fahr. (760 degrees Cent.), uniformly so adjusted that the purely thermal stresses would be identical for all. This curve represents a steel fairly sensitive to cracking;[10] some steels are worse, many are much less prone to cracking, but this example is representative of the trend toward more severe microscopic cracking with coarser austenitic grain.

[10]The analysis of the steel of Fig. 6 is as follows:

C	Mn	Si	S	P
0.94	0.40	0.133	0.044	0.034

For another somewhat more sensitive steel,[11] Fig. 7 shows the relation between the aggregate length of the cracks per unit of area and the impact strength (foot-pounds absorbed in breaking an unnotched round 0.180-inch in diameter) at a uniform hardness of Rockwell C 50. This figure well illustrates the correlation between micro-cracking and impact in a steel as variously coarsened but uniformly quenched; at the moment no very satisfactory method of controlling the severity of cracking, other than grain-size control, has been discovered. To verify this correlation, one requires a series of specimens entirely free from macroscopic cracks but covering a range, so far as the prevalence of microscopic cracks is concerned. The constant temperature method of austenite transformation at temperatures above some 400 degrees Fahr. (205 degrees Cent.) eliminates cracking altogether, and therefore exemplifies only the extreme case of zero cracks. To fulfill the experimental requirements, it is only necessary to heat the several specimens of a suitable steel at a series of temperatures, e.g., 1400, 1550, 1700, and 1850 degrees Fahr. (760, 840, 930, and 1010 degrees Cent.), then cool them to the standard quenching temperature, 1400 degrees Fahr. (760 degrees Cent.) and harden and temper.

One may conclude from the evidence of Figs. 6 and 7 that the martensite formed from increasingly coarser austenite is more and more susceptible to cracking and that impact strength decreases rapidly with the prevalence of cracks or with increase in grain-size, or both. Certainly one cannot distinguish here—any more than in a number of other cases—whether or not grain growth is a primary cause or an accompaniment to certain more fundamental phenomena which profoundly alter the properties of a steel. However, a fairly effective disentanglement of the factors involved here may be accomplished by studying in the same steel the influence of grain-size alone, i.e., in the absence of cracks, and the influence of grain-size accompanied by the cracking which increases in severity with the grain-size. For this purpose the steel of Fig. 7 was treated to produce a Rockwell C hardness of approximately 50, by the two methods contrasted in Fig. 5, after establishing for each process a series of four austenitic grain-sizes. The results are condensed in the chart of Fig. 8. Here again advantage is taken of the fact that a product of direct austenite transformation possessing a hardness of at least

[11]The analysis of the steel of Figs. 7, 8, and 9 is as follows:

C	Mn	Si	S	P
0.85	0.42	0.180	0.022	0.008

50 Rockwell C is free from cracks. One infers from the results that austenitic grain-size alone influences somewhat the toughness of the derived products but that the presence of increasingly severe cracking is a more potent cause of brittleness in the heat treated steel. The coarsening action of high heating temperatures affects adversely the toughness even of the specimens treated by the method

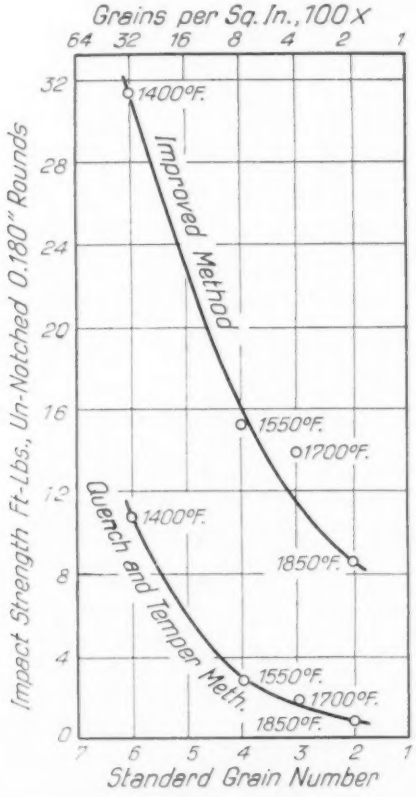

Fig. 8—Influence of Austenitic Grain-Size Upon Impact Strength of (1) Quenched and Tempered Specimens and (2) Specimens Hardened by Direct Transformation. All Quenched from 1400 Degrees Fahr. (760 Degrees Cent.) and of 50 R_c Hardness.

of constant-temperature austenite transformation wherein no cracks are developed, but the quenched and tempered steel (carrying cracks) is much more seriously injured by the coarsening treatment. In order to insure uniformity of the stresses of purely thermal origin the practice of quenching all samples from a constant temperature, 1400 degrees Fahr. (760 degrees Cent.), regardless of the coarsening temperature was employed in the tests of Fig. 8. Another study, identical except for this point, is shown in Fig. 9. In this case the

specimens for both methods were quenched directly into the respective baths from the coarsening temperature. It is significant that the results of Figs. 8 and 9 are similar; the inference is that perhaps the purely thermal stresses are not of great importance and that if any real difference exists, it favors the omission of the 1400 degrees Fahr. (760 degrees Cent.) halt. Probably in the steel used

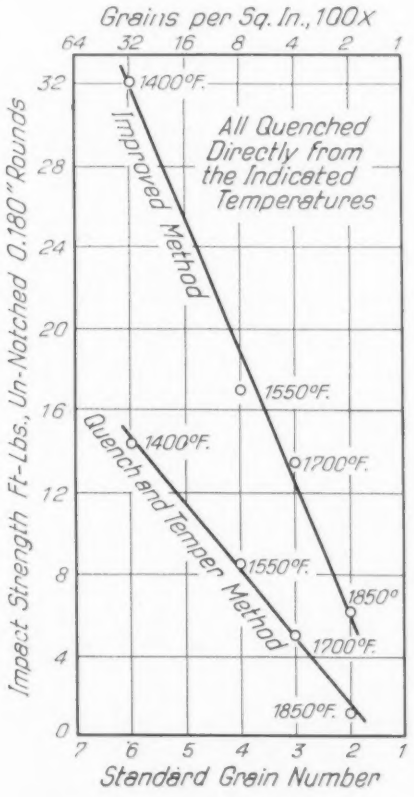

Fig. 9—Influence of Austenitic Grain-Size upon Impact Strength of (1) Quenched and Tempered Specimens and (2) Specimens Hardened by Direct Transformation. Quenched from Indicated Temperatures and All of 50 R_c Hardness.

here a trace of proeutectoid carbide formed in the grain boundaries during the halt at 1400 degrees Fahr. (760 degrees Cent.) lowering the impact strength.

Are the Cracks Present in Quenched Steel?

While the cracks have been referred to as existing in the hardened steel it has in fact not been possible to answer this question

with certainty; the evidence certainly does not prove that the cracks are absent in the freshly quenched steel prior to etching for microscopic study. Lucas[12] states: "The cracks develop by etching and only those which are relatively large can be seen in the unetched specimen," but he also expresses the opinion that they are truly cracks and not merely lines of strain opened up by the etching. The present study has given no direct evidence that the truly intragranular quenching crack is visible prior to etching, but the action of the polishing to form a "smeared" layer of metal would certainly be expected to close over any such minute ruptures and obscure them if present. This sort of reasoning, then, cannot resolve the ambiguity.

It is somewhat more significant that a steel infested with such cracks was found by Lucas still to reveal them upon etching after a tempering for 2 hours at 400 degrees Fahr. (200 degrees Cent.). But the creep limit of hardened steel at 400 degrees Fahr. (200 degrees Cent.) is still sufficiently high to permit great stress to remain in Lucas' tempered specimens and it has seemed far more important in this inquiry to temper the quenched, and hence potentially cracked, steel to such a temperature as would reduce the possible residual stress to a negligible, or an extremely low, value. If then such specimens, upon etching, reveal any typical microscopic ruptures, the evidence would be more satisfying for the reality of the cracks in the quenched steel, for it seems unlikely that etching alone could release stresses of any magnitude and thus cause cracking in such softened material. That the cracks may be present in some specimens in which the original martensite has been converted to the extremely soft condition of spheroidized carbide in ferrite may be seen in Fig. 10. The high tempering temperature (2 hours at 1300 degrees Fahr., 705 degrees Cent.), used in spheroidizing the martensitic specimen, caused a final hardness of only about 150 Brinell. It would appear significant enough that such a thorough subcritical anneal fails to remove the cracking, but as a matter of fact, the micro-cracks formed in the martensite persist even when the steel is heated above the critical range and thereby rendered austenitic. Cracks are clearly seen in Figs. 11 and 12 which are photomicrographs of originally martensitic specimens heated respectively to 1550 and 1800 degrees Fahr. (845 and 980 degrees Cent.) and then so cooled therefrom as to permit spheroidi-

[12]See Footnote 3.

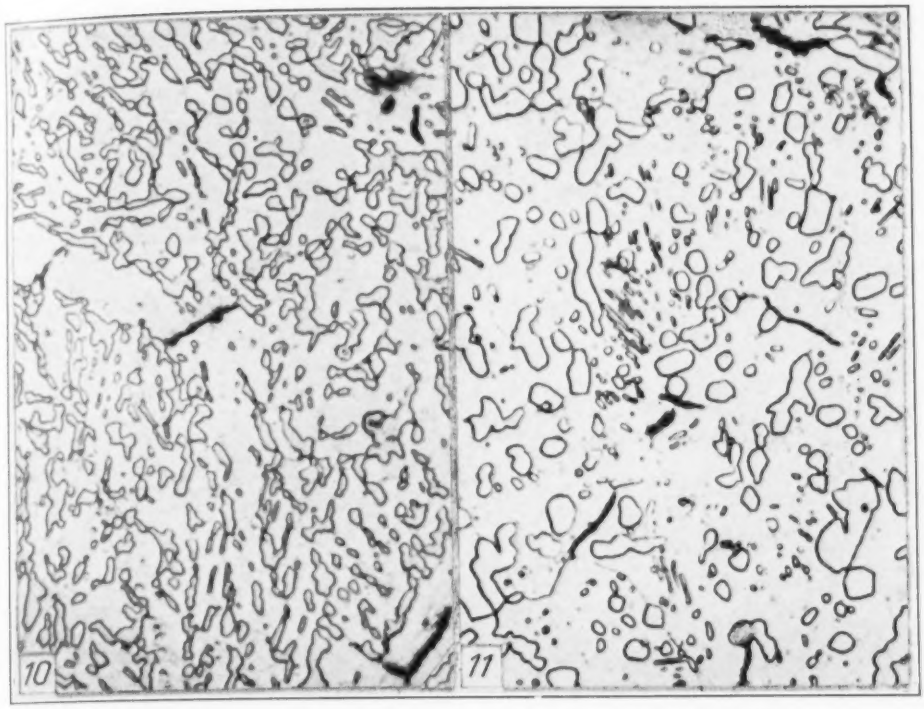

Fig. 10—The Persistence of Micro-Cracks in Sub-Critically Spheroidized Martensite. × 1200.

Fig. 11—The Persistence of Micro-Cracks in Originally Martensitic Steel Heated to 1550 Degrees Fahr. (845 Degrees Cent.) and Spheroidized Before Cooling. × 1200.

zation. In these specimens the cracks were produced upon quenching from 1725 degrees Fahr. (940 degrees Cent.) and the subsequent slow heating and slow cooling failed to eliminate them. In some instances a heating to 2000 degrees Fahr. (1100 degrees Cent.) caused the cracks in the original martensite to close up completely and the metal apparently to weld. All these specimens with the persistent cracks were of a high carbon steel which developed an extraordinarily coarse austenite grain.

Clearly the spheroidized steel carried no stresses sufficiently high to cause micro-cracking upon etching, for if this were possible then annealed steel must often manifest micro-cracks. The inference is drawn that in some extreme cases the micro-cracks are actually formed in the martensite prior to etching, probably only in coarsened steel. In the general case, the micro-cracks probably rather more often mark the location of the highest stress concentrations, sufficiently high, presumably, to cause micro-cracking upon a slight subsequent shift in the balance of stresses. To the authors it appears probable that the etching (or, more unlikely, the grinding

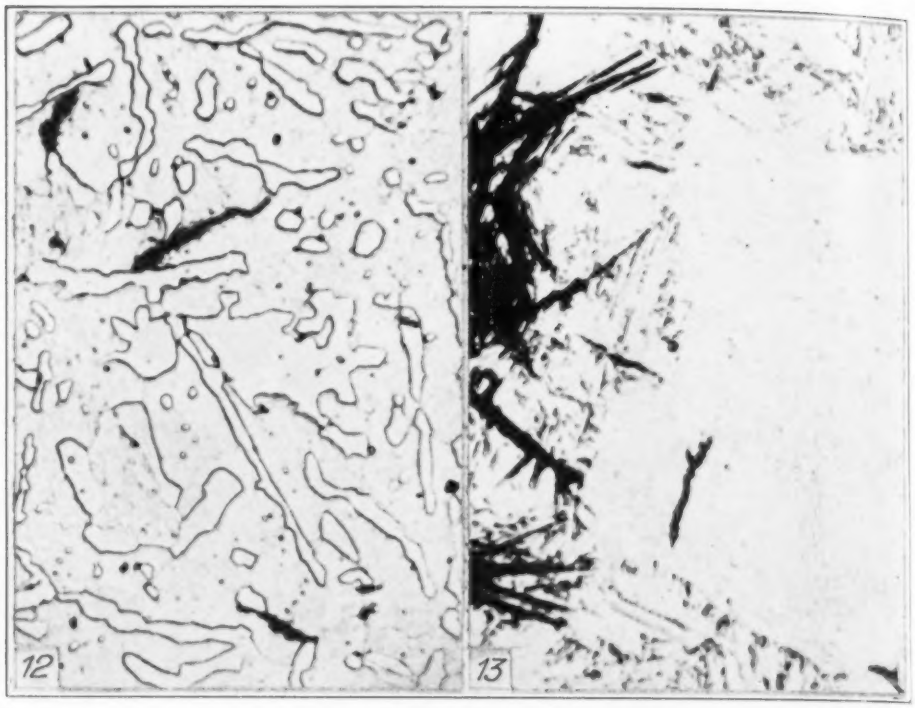

Fig. 12—The Persistence of Micro-Cracks in Originally Martensitic Steel Heated to 1800 Degrees Fahr. (980 Degrees Cent.) and Partially Spheroidized Prior to Slow Cooling. × 1200.

Fig. 13—Micro-Cracks in the Martensite of a Specimen Partially Transformed at 400 Degrees Fahr. (200 Degrees Cent.) and Quenched Therefrom into Brine. × 1200.

or polishing) usually provides the opportunity for the stresses to be relieved by the cracking of the steel.

It is a fortunate circumstance, even though it has been a puzzling one, that martensite, which shows micro-cracks upon etching, is usually really tough when tempered to a hardness of about 40 C Rockwell or less, nearly as tough indeed as the crack-free product having the same hardness. The inference is that the stresses, high in the martensite, diminish gradually with the tempering; conceivably, the minute cracks occasionally opened up in the martensite prior to etching may not cause much embrittlement in a material from which stress has been largely removed.

As a matter of fact, very little practical importance attaches to the question of the reality of the cracks prior to etching; the high stress concentration necessary for their immediate appearance after etching would for practical purposes be as serious a problem as the cracks themselves.

Observations on the Formation of Micro-cracks

It is perhaps of interest to consider the development of the quenching cracks from another viewpoint. It has been pointed out that no cracks develop when austenite completely transforms to a slightly softer product than martensite, for example, the acicular troostite product of about 50 C Rockwell, employed in the impact studies. In this case the transformation in a 0.74 per cent carbon steel occurred at about 600 degrees Fahr. (315 degrees Cent.) and required about 15 minutes for completion. If now the constant-temperature transformation method is applied to a 1.15 per cent carbon steel at a constant temperature of about 400 degrees Fahr. (200 degrees Cent.) the transformation will require between 15 and 20 hours for completion and the product will possess a Rockwell hardness of about 63 C. But even in this case the product of complete transformation is not martensite and possesses no discoverable micro-cracks. During this fifteen hour interval while the specimen is in the constant temperature bath at 400 degrees Fahr. (200 degrees Cent.) the proportion of austenite remaining is gradually diminishing. At any moment the specimen may be removed and cooled, to room temperature for example, and the untransformed austenite will instantly change to martensite. Now while no cracks are ever found in the product characteristic of a transformation *completed* at 400 degrees Fahr. (200 degrees Cent.), nevertheless, generally speaking, the martensite of such a steel is subject to quenching cracks. It may therefore be interesting to see whether or not martensite develops cracks when formed by quenching from about 400 degrees Fahr. (200 degrees Cent.) instead of from the usual supercritical temperatures. Fig. 13 shows the structure developed when the slow transformation at 400 degrees Fahr. (200 degrees Cent.) is interrupted by quenching the sample into brine while some 80 per cent, more or less, of the austenite is still unchanged. This 80 per cent then transforms to martensite, nearly white in the photomicrograph. The product of the 400 degrees Fahr. (200 degrees Cent.) transformation is revealed as a dark-etching acicular constituent. A few cracks are to be found in the martensite of such a specimen and at least 2 or 3 are visible in the photomicrograph. Actually it is found that if the transformation at the elevated temperature, e.g., 400 degrees Fahr. (200 degrees Cent.) proceeds much beyond this extent, until perhaps some 40 per cent has transformed,

then cracking is not discovered in the martensite. The situation is similar in another type of mixed structure; cracks may be seen in the martensite associated with the nodular fine-pearlite (sometimes called quenching troostite) of specimens quenched just under the critical quenching rate; if, however, the proportion of fine-pearlite is fairly large no cracks are in evidence. Only very few, if any, cracks have been found in the martensite which forms a part of the quenched structure in steels carrying about 0.6 to 1.2 per cent carbon with from 6.0 to 2.0 per cent manganese. These steels readily retain a large proportion of very persistent austenite and, as quenched, are composed therefore wholly of hard martensite and soft austenite; they constitute a group, lying, so to speak, midway between the two familiar classifications of manganese steels, frequently designated in the literature as martensitic and as austenitic respectively.

Now in all these cases hard martensite is associated with a plastic substance, fine pearlite, acicular troostite, or austenite, capable of some deformation. It seems therefore possible that when the complex dimensional changes accompanying the formation of martensite can be accommodated by a considerable amount of plasticity in another well distributed phase, the highest stresses in the martensite can be avoided and hence rupture is prevented. In the case of quenched high carbon steels in which coarse-grained austenite has been produced by excessively high heating temperature, cracks are definitely present in the martensite, in spite of the presence of even 40 to 50 per cent retained austenite; here grain-size is evidently exerting a dominant influence.

It has been noted that a majority of the cracks run approximately at right angles to the principal axis of the needles or plates of martensite, the regions which, it appears, are the first to transform.[13] It may therefore be inferred that the stress is one of tension in the axis of the needle, or, more probably, in one direction of the plane of the first plates. In reconstructing the mechanism[14] of

[13]H. Hanemann, U. Hofmann und H. J. Wiester, "Die Gefügeänderungen des Stahles beim Härten und Anlassen," Archiv. Eisenhüttenwesen, 1932-1933, Vol. 5, p. 199. Also see Footnote 2.

[14]Two possibilities at least come to mind: (1) If the orientation of a plate of martensite (viewed as a needle on the polished section) were such as to correspond with a shortened axis of the original austenite the rupture would occur before the remainder of the austenite grain transformed, for the compressive stress borne by the large unchanged regions would not cause much compressive deformation therein, and the plate must be severed by tension. However, in the manganese steels in which only a few such plates of martensite form upon quenching no cracks are formed; another mechanism must be sought. (2) If the first needles form with orientation such as to involve strong expansion along an axis, then some flow in the surrounding plastic austenite would occur, and

building up stresses sufficient, finally, to pull apart a plate of martensite this circumstance should be borne in mind.

Before summarizing the various points of this paper, one more observation should perhaps be mentioned. When gross quenching cracks, resulting in a thoroughly defective piece, are examined microscopically they are usually found to be dominantly intergranular with respect, of course, to the original austenite. If one follows such a representative macroscopic rupture inward from the surface it is frequently found to end in many intercrystalline branches. It is therefore inferred that the large cracks result from stress of wide extent and that they are formed somewhat differently from the true micro-cracks. In the first place, they are probably formed at a later time than the microscopic ones. Steels sensitive to micro-cracking seem also prone to gross cracking, and one is led to believe that dimensional changes during transformation, in a statistical sense rather than in specific crystal directions, produce the widespread stresses responsible for the macroscopic cracks.

The intragranular stresses, although of very narrow space distribution, may be of high intensity, for along certain crystalline directions the unrestrained linear change of dimension during transformation might possibly amount to 20 or 25 per cent. If the actual distance involved in such contractions and expansions is small, a moderate degree of plasticity may prevent rupture; but if a greater distance within the individual austenite grain is involved, the stress must be tremendously high. The block of unit cells involved in a single martensite orientation or a single transformation-step is probably small in a fine-grained austenite and large in a coarser grained austenite; if so, the greater tendency for micro-cracks in the coarsened steels is easily explained. The circumstance of cracks in the first plates or needles, and the step-wise formation of martensite are probably the most significant factors.

Summary

Many carbon steels after severe quenching exhibit, upon etching, a characteristic system of microscopic, intragranular cracks across the original needles or plates of the martensite. Tempering does not appear to obliterate wholly the stresses responsible for these

the needle or plate would be in moderate compression. Finally, when the remainder of the grain transforms the general expansion would probably be sufficient to rupture the nonductile martensite now in tension. The data of the crystal physics of martensite formation is being so rapidly developed by experimenters such as Mehl, Sachs, Wever, Hanemann and others that some of these problems will probably be clarified in the near future.

cracks. A method of producing crack-free steel with the hardness of only moderately-tempered martensite is explained. The micro-cracks contribute brittleness to the heat treated carbon steels as shown by comparisons with crack-free specimens of the same steel produced, not by full hardening followed by tempering, but by direct and complete transformation of the austenite at moderately elevated constant temperature.

The severity of the micro-cracking, and the consequent lowering of ductility, increases with the grain-size of the austenite from which the tempered martensite is developed in the heat treating. Large austenitic grain-size has an injurious effect upon the ductility even of crack-free hardened steel, but the effect of the micro-cracks is large in comparison with the influence of grain-size alone.

The presence, in suitable amount, of a well-distributed soft constituent (such as fine pearlite resulting from low quenching rate, acicular troostite from incomplete transformation at elevated constant temperatures, or possibly retained austenite in alloy steel) eliminates the micro-cracks in the martensite. At the very least 25 per cent of the softer constituent seems to be necessary; in the case of a coarse austenitic grain-size cracks may form in spite of the presence of the softer constituent.

The superior toughness of many heat treated alloy steels is believed to be due to the absence of micro-cracks brought about by the characteristically fine, austenitic grain-size. The necessary hardening capacity, to offset the shallow-hardening influence of small grain-size, is imparted to the steel by the alloying element, while the fine grain is itself preserved by the same alloying elements, by another element, or by the deoxidation technique.

The micro-cracks are believed to result from the large dimensional changes, within an individual austenite grain, accompanying its step-wise transformation to martensite. Along certain directions in the austenite crystal large linear expansion or contraction occurs over the range of a block of unit cells all transforming in one orientation relationship. The gross volume change is itself relatively large and sets up dangerous general stresses of broad distribution, which may result in gross cracking. The intragranular stresses, which may be very much higher, are believed to be responsible for the micro-cracks.

THE TORSION IMPACT PROPERTIES OF HARDENED CARBON TOOL STEEL

By G. V. Luerssen and O. V. Greene

Abstract

The development of an impact test applicable for use with hardened and slightly tempered carbon steels is briefly outlined. In this test, specimens are fractured under torsional impact. Torsion impact data obtained upon three carbon tool steels are included. It is shown that there are peaks of maximum toughness in hardened carbon tool steel occurring at relatively low drawing temperatures, the positions of which can be altered by varying treating conditions, such as heating media, quenching temperature, and drawing time. The effect of an inherent characteristic, such as timbre, on steels of the same analysis and the influence of variable carbon content is included. Suggestions as to the causes of these peaks of maximum toughness are offered.

Introduction

IT IS generally assumed that low ductility materials such as hardened or slightly tempered carbon tool steels have relatively poor characteristics when used or tested under conditions of dynamic loading. However, service results indicate that there is a wide variation in the shock resistance of such steels when treated to identical hardness values. Furthermore while the significance of the impact test on ductile materials is definitely established, attempts to correlate serviceability and test data obtained by the usual methods on these extremely hard materials, have in general been abortive.[1]

It is obvious therefore that there is a vast field of usefulness for an impact test that will quantitatively differentiate low ductility materials. An impact machine that has been successfully used for this purpose has been previously described.[2]

[1]Symposium on Impact Testing of Materials, Proceedings of A. S. T. M., Vol. 22, 1922.

[2]G. V. Luerssen and O. V. Greene, "The Torsion Impact Test." Paper presented at 36th Session of A. S. T. M., Chicago, June, 1933.

A paper presented before the Fifteenth Annual Convention of the society held in Detroit October 2 to 6, 1933. The authors are members of the society and are associated with the metallurgical department of the Carpenter Steel Co., Reading, Pa. Manuscript received July 27, 1933.

Description of Steels Investigated

It is the purpose of this paper to record the torsion impact data obtained on two types of carbon tool steel. One type is a general purpose tool steel containing approximately 1.05 per cent carbon. The other is a 0.90 per cent carbon heading die steel. The former is in two timbres,[2a] to illustrate the effect of this characteristic on the behavior of such steels. The analyses of these three steels are given in Table I.

The results of the timbre tests on the three steels are shown in Fig. 1, which includes sections of ¾-inch round bars brine-quenched

Table I

Analyses of Carbon Tool Steels

	Per Cent						
	C	Mn	Si	P	S	Cr	Ni
Tough Timbre Steel	1.06	0.20	0.16	0.010	0.012	0.03	0.04
Brittle Timbre Steel	1.03	0.23	0.16	0.019	0.017	0.06	0.10
Heading Die Steel	0.90	0.45	0.50	0.014	0.009	0.08	0.08

from 1450, 1500 and 1550 degrees Fahr. The sections on the upper half are actual fractures. Those below correspond but with the section ground and etched in 1:1 HCl to bring out the hardness penetration. The bars were all annealed to a spheroidized structure and had Brinell hardnesses of 160 to 165. A marked variation in quenching characteristics is apparent; although the 1.06 per cent carbon tough timbre and the 1.03 per cent carbon brittle timbre steels are of practically identical analysis, their fractures and penetrations are quite different. The tough timbre steel has a shallow case and a silky case fracture throughout the range of quenching temperatures used. On the other hand the brittle timbre steel has a slightly coarser fracture, with a somewhat deeper case even when quenched from 1450 degrees Fahr. After quenching from 1500 degrees Fahr. these characteristics are considerably accentuated. The brittle timbre steel after brine quenching from 1550 degrees Fahr. has become very coarse and hardens nearly through the section.

The heading die steel is of a tough timbre type and has a fine, silky case fracture, with somewhat deeper hardness penetration at all of the quenching temperatures.

[2a] G. V. Luerssen, "Some Notes on the Behavior of Carbon Tool Steel on Quenching." Transactions, American Society for Steel Treating, Vol. 17, No. 2, 1930, p. 161.

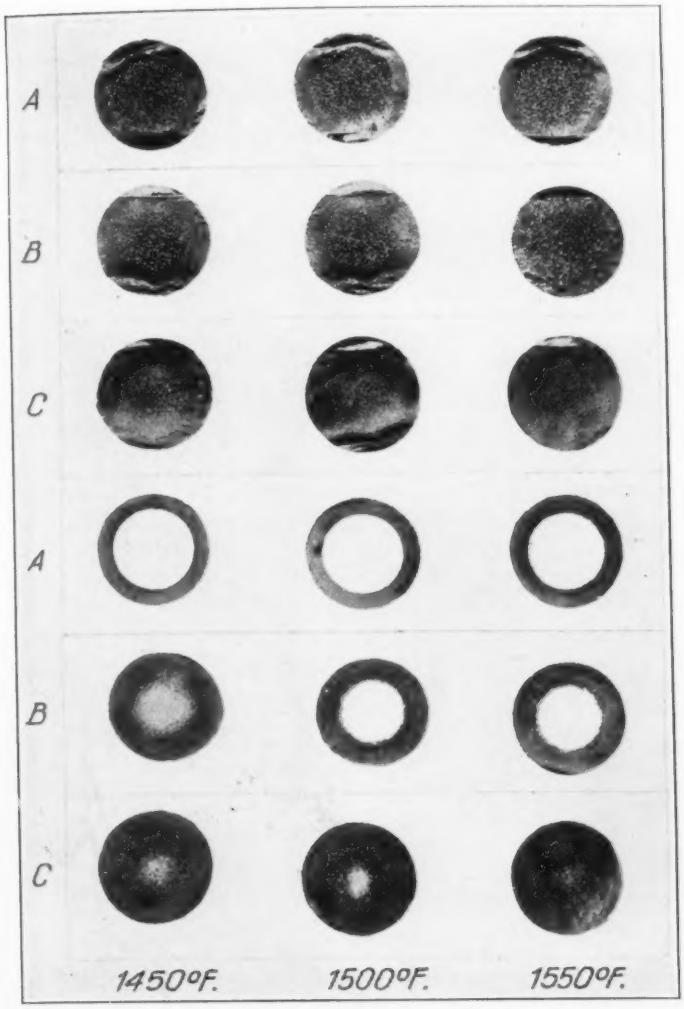

Fig. 1—Sections of Three Steels Quenched from Three Different Temperatures in Brine. The Upper Group Shows the Actual Fractures. The Lower Group Shows Corresponding Sections Ground and Etched to Bring Out Hardness Penetration. A—1.06 Per Cent Carbon Tough Timbre Steel; B—1.03 Per Cent Carbon Brittle Timbre Steel; C—0.90 Per Cent Carbon Heading Die Steel. Actual Size.

The Test Machine and Method

The records of previous work upon the impact testing of hard materials are but meager. Barry,[3] Grossmann,[4] Margerum[5] and

[3]R. K. Barry, "Hardness and Toughness of High Speed Steel as Affected by Heat Treatment," Transactions, American Society for Steel Treating, Vol. 10, 1926, p. 257. "Comparisons of Impact and Slow Bend Tests of High Speed Steel," Transactions, American Society for Steel Treating, Vol. 12, 1927, p. 630.

[4]M. A. Grossmann and E. C. Bain, "High Speed Steel," John Wiley & Sons, 1931, p. 140.

[5]C. E. Margerum, "A Test for Shock Strength of Hardened Steel," *Proceedings*, American Society for Testing Materials, Vol. 21, 1921, p. 876.

Styri[6] have contributed information. A study of previous methods shows that in general notched or unnotched transverse, or unnotched tension bars were employed. All of these methods employ suddenly applied loads with the resulting stresses localized in varying degrees

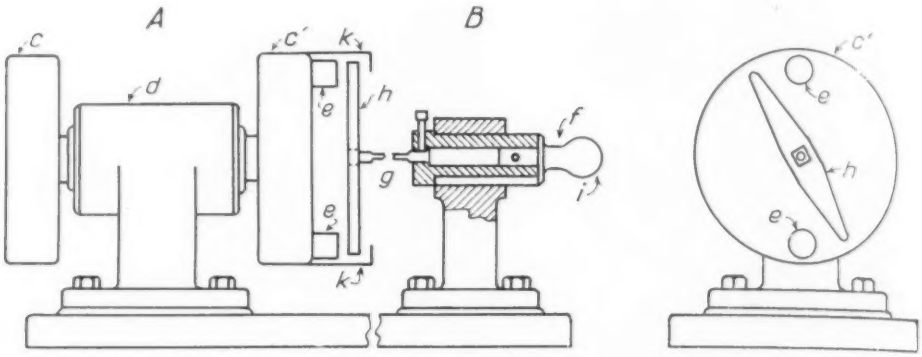

Fig. 2—Sketch of Torsion Impact Machine.

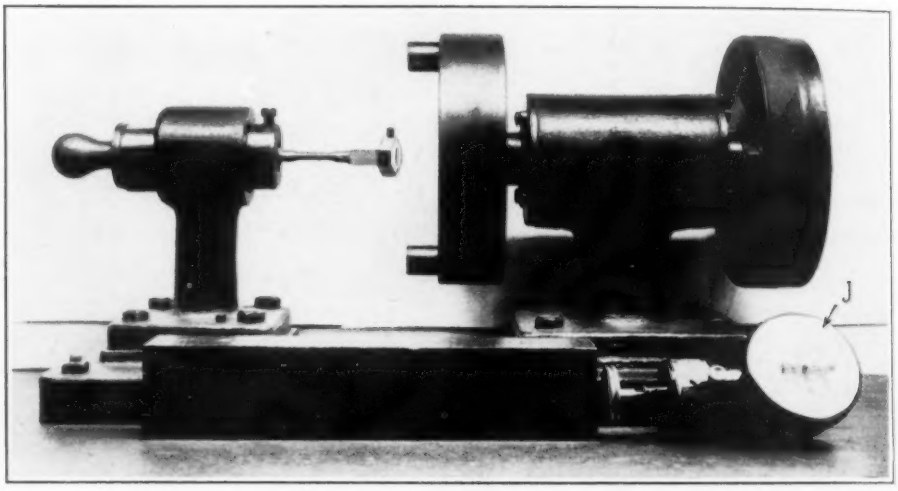

Fig. 3—View of Torsion Impact Machine and Specimen Ready for Test.

depending upon the design of the specimen and notch. The influence of design of specimen and notches has been very completely covered by McAdam[7] and Heymans.[8]

In all of these cases, however, the stress concentration is too

[6]Haakon Styri, "Relation Between Magnetic Properties, Impact Strength and Hardness," *Proceedings*, American Society for Testing Materials, Vol. 31, Part II, 1931, p. 94.

[7]D. J. McAdam, Jr., "Impact Test of Metals," *Proceedings*, American Society for Testing Materials, Vol. 22, 1922, p. 37.

[8]Paul Heymans, "Interpretation of Notched Bar Impact Test Results," TRANSACTIONS, American Society for Steel Treating, Vol. IX, 1926, p. 604.

great to allow accurate measurement of impact values of extremely hard, low ductility materials. Consequently the authors have devised a method employing the torsion principle which provides a means of sufficient stress distribution to facilitate measurement. The designs of the impact machine and specimen contrived for this purpose are

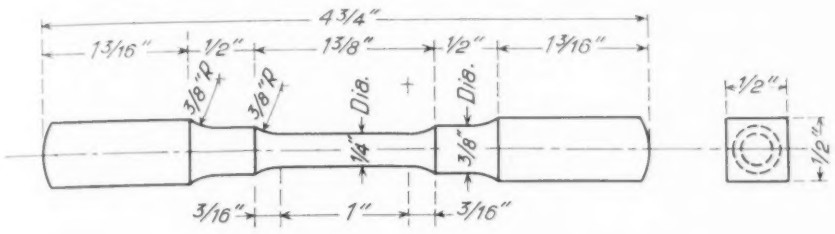

Fig. 4—Details of Torsion Impact Specimen.

given in Figs. 2, 3 and 4. From Fig. 2 it may be seen that the machine consists of two parts, a momentum unit, A, and a head, B, for holding the specimen. The momentum unit consists of two balanced fly wheels, c and c′, mounted on a shaft rotated in ball bearings housed in d. The fly wheel, c′, contains two striking bosses, e. The fly wheels are rotated by means of a friction wheel driven by a portable motor on the periphery of c. The movable head, B, is made up of a sleeve, f, having a square hole in one end, into which the head of the specimen, g, is clamped by means of a set screw. The opposite end of the specimen is attached to a cross arm, h. The sleeve, f, can be slid axially by the knob, i.

The actual method used in making a test is essentially as follows: The specimen is clamped in the sleeve, f, with the cross arm, h, attached. The knob, i, is pulled back so that the cross arm, h, clears the bosses, e. The fly wheels are then rotated to a predetermined speed, measured by a portable tachometer, j, driven on the periphery, c. The knob, i, is then pushed inward, engaging the cross arm with the bosses, and the specimen is thus broken in torsion impact. The residual speed is read, from which the energy absorbed can be easily obtained.

Fig. 3 shows the machine and specimen ready for test. A guard of thin sheet metal, k, is attached to the fly wheel, c′, which prevents the cross arm from flying after the specimen is broken. This has been removed in Fig. 3 to simplify description. The details of the specimen used are shown in Fig. 4.

Test Data

By means of the torsion impact machine it has been possible to show the point of maximum toughness in hardened and slightly tempered carbon tool steels, the position of which may be altered at will by varying the treating conditions. The effect of heating media, quenching temperature, drawing time and inherent characteristics such as timbre on this peak will be described in the following paragraphs:

Influence of Quenching Temperature and Timbre—The torsion impact results and C Rockwell hardnesses for various quenching and drawing temperatures on the three steels used in this work are given in Tables II, III and IV. Fig. 5 shows these data with the torsion impact in foot-pounds plotted as ordinates and drawing temperature, degrees Fahr., as abscissae. The average values used were based on at least duplicate and in many cases five tests at each quenching and drawing temperature. The specimens were machined from ½-inch square bars, spheroidized annealed, and had Brinell hardnesses of 160 to 165. Photomicrographs of these structures are shown in Figs. 11, 12 and 13.

In order to eliminate as many variables as possible, all of the specimens included in this portion of the investigation were preheated at 800 degrees Fahr. in an electric muffle, transferred to a lead pot, and heated to the quenching temperature used, held at this temperature for five minutes, and quenched in a 15 per cent brine solution held between 90 and 100 degrees Fahr. The temperature of the quenching medium may seem extraordinarily high. However, it was found impossible to successfully quench the brittle timbre specimens, particularly from 1500 or 1550 degrees Fahr. in brine at room temperature (60 to 70 degrees Fahr.). At these quenching temperatures all of the brittle timbre specimens cracked. However, raising the brine temperature to 90 to 100 degrees Fahr. eliminated the trouble, so that only one specimen out of every ten or fifteen cracked. All specimens were drawn for one hour in oil at the temperatures shown, and cooled from the draw in the air. Undrawn specimens were held 24 hours at room temperature before testing.

The type of impact curves obtained is very striking. The 1.06 per cent carbon tough timbre steel after brine quenching from 1450 degrees Fahr. shows 29 foot-pounds and 67-C Rockwell. The toughness exhibited by material of this hardness is quite unexpected. Slight

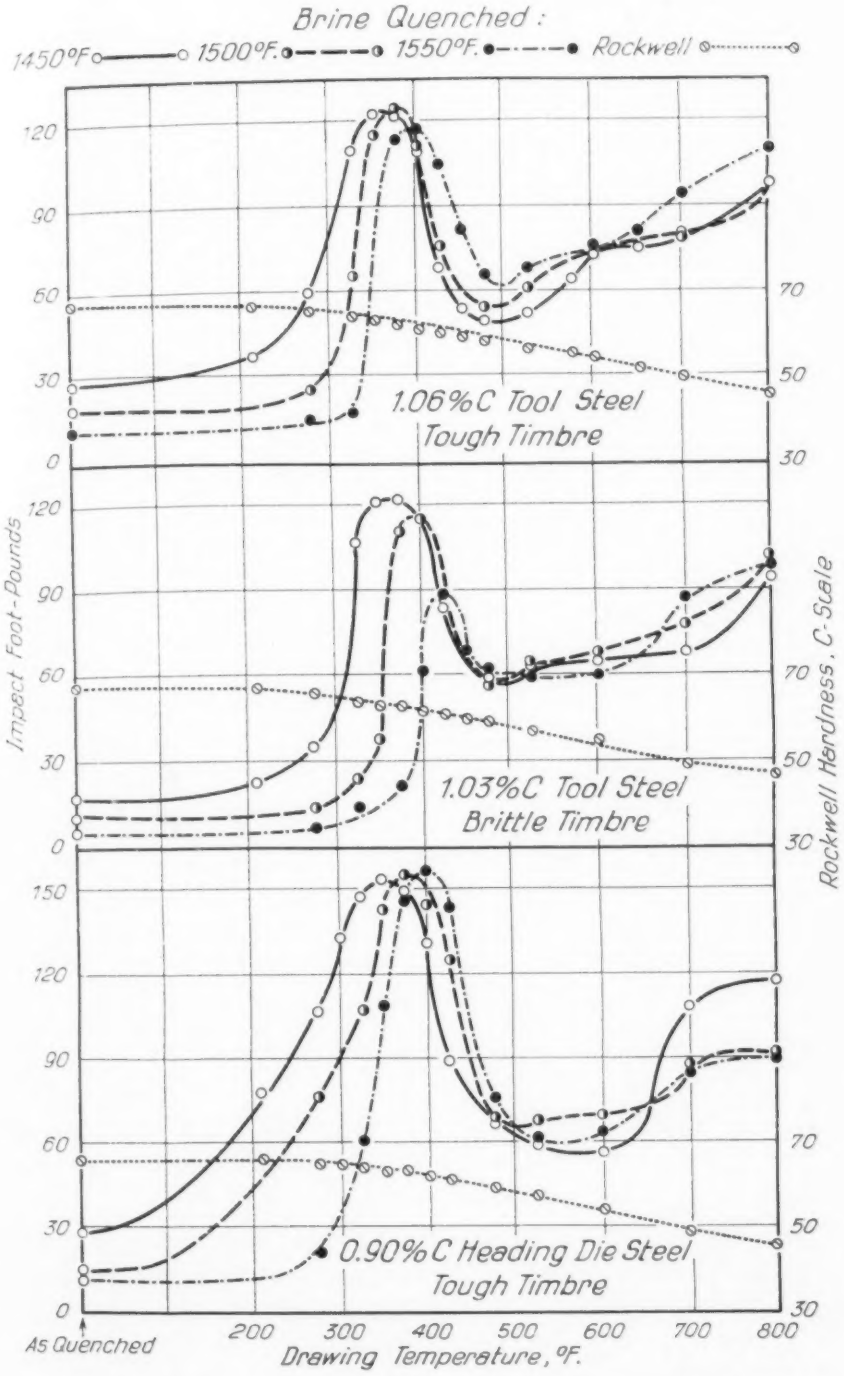

Fig. 5—Torsion Impact Results and C Rockwell Hardnesses for Various Quenching and Drawing Temperatures on Three Steels. This Chart Shows Effect of Quenching Temperature on Location of Peaks. All Specimens Quenched in Brine from the Lead Pot and Drawn for One Hour at Temperatures Indicated.

Table II
Influence of Quenching Temperature
Torsion Impact Results on 1.06 Per Cent Carbon Tough Timbre Steel
Brine-Quenched from the Lead Pot and Drawn One Hour at Indicated Temperatures

Drawing Temperature Degrees Fahr.	Brine Quenched From 1450 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness	Brine Quenched From 1500 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness	Brine Quenched From 1550 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness
As quenched	29	67.0	18	66.7	11	66.5
212	37	66.8	..	....	..	....
275	60	66.5	26	65.5	15	65.5
325	112	65.0	66	64.0	18	64.2
350	123	64.0	117	63.8	..	....
375	122	63.0	124	63.4	108	63.0
400	111	62.2	113	62.3	118	62.3
425	70	61.2	77	61.3	105	61.4
450	54	60.2	..	....	83	60.5
475	50	59.8	56	59.5	66	59.8
525	52	57.8	63	58.6	68	57.0
575	64	56.0	..	....	..	....
600	74	54.7	73	55.1	74	56.5
650	75	52.0	..	....	81	52.5
700	79	49.6	78	50.5	94	50.8
800	98	46.0	99	46.5	109	46.2

Note: Impact values are average of at least duplicate tests and C Rockwell hardnesses are average of 20 determinations.

drawing increases the impact value rapidly until a maximum is reached at 350 degrees Fahr. After this point is passed the values fall off sharply until 475 degrees Fahr. is reached. Beyond this minimum the impact values increase with drawing temperature. The curves of the 1500 and 1550 degrees Fahr. quench show similar peaks. However, attention is drawn to the fact that the energy values as quenched are correspondingly lower and that the peaks progress slightly to the right, i.e., the peak of the series brine-quenched from 1500 degrees Fahr. is found at 375 degrees Fahr., and brine-quenched from 1550 degrees Fahr. is found at 400 degrees Fahr. It is interesting to note that these peaks are similar to those shown by Emmons[9] for a steel containing 1.12 per cent carbon and 1.07 per cent chromium. In Emmons' work coefficients of toughness are plotted as ordinates and drawing temperatures as abscissae.

The curves of the 1.03 per cent carbon brittle timbre steel exhibit similar maximum peaks. However, the tests in the as quenched condition are considerably lower than the 1.06 per cent carbon tough timbre steel. The peak of the 1450 degrees Fahr. quench occurs at 375 degrees Fahr.; the 1500 degrees Fahr. quench at 400 degrees Fahr., and the 1550 degrees Fahr. quench at 425 degrees Fahr. As

[9]J. V. Emmons, "Some Physical Properties of Hardened Tool Steel," *Proceedings*, American Society for Testing Materials, Vol. 31, Part II, 1931, p. 47.

Table III
Influence of Quenching Temperature
Torsion Impact Results on 1.03 Per Cent Carbon Brittle Timbre Steel
Brine-Quenched from the Lead Pot and Drawn One Hour at Indicated Temperatures

Drawing Temperature Degrees Fahr.	Brine Quenched From 1450 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness	Brine Quenched From 1500 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness	Brine Quenched From 1550 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness
As quenched	16	66.8	11	66.2	5	66.0
212	21	66.5	..	....	..	....
275	34	66.0	14	65.5	6	65.2
325	107	64.8	24	64.2	12	64.0
350	122	64.0	38	63.7	..	....
375	125	62.5	112	62.8	21	62.7
400	110	62.5	114	62.4	61	61.8
425	85	61.7	87	61.6	89	61.3
450	..	....	..	....	69	61.2
475	58	59.9	57	59.7	62	59.8
525	66	57.8	63	57.8	60	57.7
600	64	56.0	67	56.0	60	56.2
700	67	51.2	78	50.5	87	49.0
800	95	47.0	102	47.0	99	46.8

Note: Impact values are average of at least duplicate tests and C Rockwell hardnesses are average of 20 determinations.

Table IV
Influence of Quenching Temperature
Torsion Impact Results on 0.90 Per Cent Carbon Heading Die Steel
Brine-Quenched from the Lead Pot and Drawn One Hour at Indicated Temperatures

Drawing Temperature Degrees Fahr.	Brine Quenched From 1450 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness	Brine Quenched From 1500 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness	Brine Quenched From 1550 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness
As quenched	28	66.7	15	66.8	12	66.3
212	67	66.4	..	....	..	....
275	113	65.2	75	65.0	22	65.4
300	132	64.8	..	....	..	....
325	147	64.3	107	64.1	60	64.2
350	154	63.4	143	63.2	109	63.9
375	149	62.4	155	62.8	145	62.1
400	130	62.3	142	61.9	159	62.0
425	89	61.0	125	61.3	143	60.9
475	68	59.2	65	59.8	75	59.5
525	58	57.8	67	57.6	60	57.6
600	55	55.5	68	55.3	64	55.8
700	108	49.8	87	49.8	85	50.4
800	117	46.4	92	46.5	90	46.5

Note: Impact values are average of at least duplicate tests and C Rockwell hardnesses are average of 20 determinations.

compared to the 1.06 per cent carbon tough timbre steel, the peaks of the 1.03 per cent carbon brittle timbre steel are seen to occur at 25 degrees Fahr. higher draw for each quenching temperature respectively.

The most important feature of the curves of the brittle timbre

steel as compared to those of the tough timbre steel is the magnitude of their peaks. The peaks of the tough timbre steel brine-quenched from 1450 degrees Fahr. and from 1500 degrees Fahr. occur at practically identical impact values and drop only slightly after brine quenching from 1550 degrees Fahr. On the other hand, the data obtained at these three quenching temperatures with the brittle timbre steel show conspicuously the effect of timbre on toughness. The peaks of the brittle timbre steel are noticeably lowered by quenching from 1500 degrees Fahr. and very appreciably lowered by quenching from 1550 degrees Fahr. A direct comparison of these two steels is shown in the upper half of Fig. 7.

The impact values of the 0.90 per cent carbon heading die steel as quenched at all three temperatures are quite similar to those of the 1.06 per cent carbon tough timbre steel. Also the peaks of this steel occur at the same drawing temperatures for each quenching temperature as those of the 1.06 per cent carbon tough timbre steel. Their magnitude is, however, on the average 30 foot-pounds higher than the 1.06 per cent carbon tough timbre steel. It is also interesting to note that as the quenching temperature increases, the maximum impact value is slightly higher.

The hardness values at the peaks are approximately the same for all three steels investigated. Considering each steel separately it is evident from Tables II, III and IV that irrespective of quenching temperature the hardnesses are approximately the same when drawn at the same temperature. Consequently only average hardness curves are shown in Fig. 5. The peaks occur in general at hardness values of C-62 to C-63 Rockwell at quenching temperatures of 1450 and 1500 degrees Fahr., and at C-61 and C-62 Rockwell when brine-quenched from 1550 degrees Fahr.

The character of the fractures obtained at various points in the curves is interesting. A series of the 0.90 per cent carbon heading die steel used in obtaining the data plotted in Fig. 5 is shown in Fig. 6. The fractures as brine-quenched from 1450 degrees Fahr. and up to a drawing temperature of 325 degrees Fahr. are of the rough shattered type, often showing the characteristic 45 degrees helical torsion failure. Specimens drawn from 350 to 375 degrees Fahr. usually shear first, and then shatter. Higher drawing temperatures produce fractures of the distinctly shear type similar to those obtained on soft steels broken in static torsion. At the higher quenching temperatures fractures up to the peaks are rough. When the peaks are

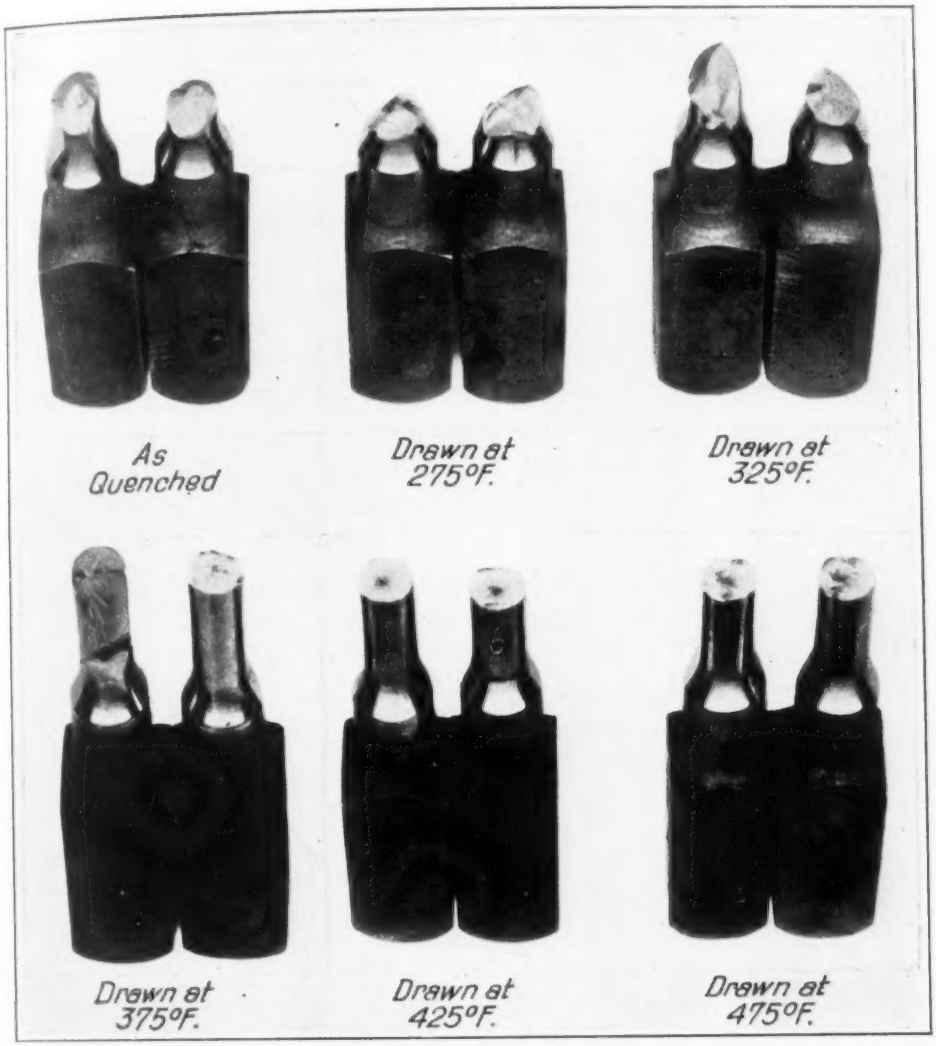

Fig. 6—The Characteristics of the Fractures of Specimens of 0.90 Per Cent Carbon Heading Die Steel, Brine-Quenched from the Lead Pot at 1450 Degrees Fahr. and Drawn as Shown.

reached, tests first shear and then shatter. After the peak is passed, they exhibit the shear type of failure.

The microstructures of the 1.06 per cent carbon tough timbre steel brine-quenched from 1450 degrees Fahr. and drawn from 275 to 425 degrees Fahr. in 25-degree intervals, omitting the 300 degrees Fahr. draw, are given at 1500 diameters in Figs. 14 to 19 inclusive. The structure at the peak for this quenching temperature, which is 350 degrees Fahr., is composed of martensite. At 375 degrees Fahr. the martensitic needles in the matrix are beginning to darken in patches. This condition increases with increase of drawing temper-

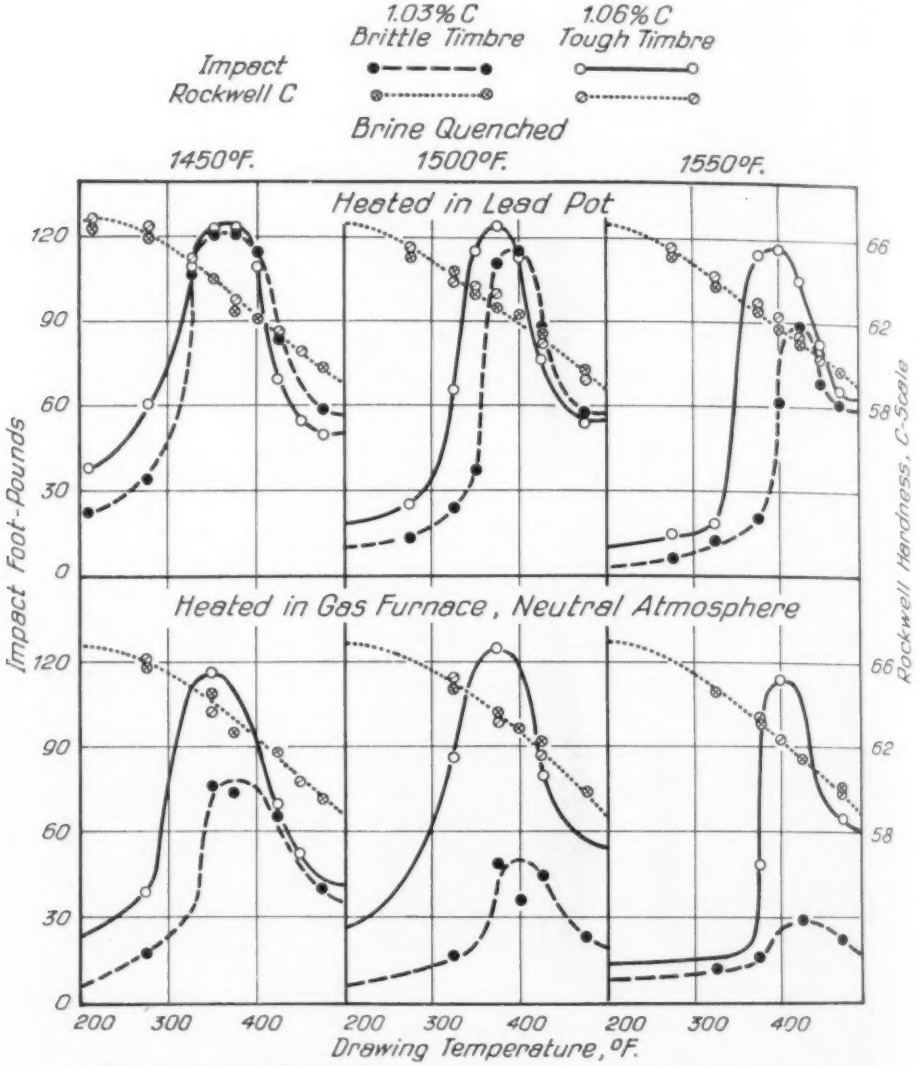

Fig. 7—Torsion Impact Results and C Rockwell Hardnesses on the 1.03 Per Cent Carbon Brittle Timbre and 1.06 Per Cent Carbon Tough Timbre Steels, Heated in the Lead Pot, and in the Gas Furnace with Neutral Atmosphere, Quenched from the Temperatures Indicated, and Drawn One Hour at the Temperatures Shown.

ature. Micrographs of specimens of this steel brine-quenched from 1500 degrees Fahr., and drawn at 275, 325 and 375 degrees Fahr. are shown in Figs. 20 to 22 inclusive. The microstructure of the peak of this curve which occurred at 375 degrees Fahr. is seen to be composed of martensite and a few darkened needles. The microstructure of the specimen brine-quenched from 1550 degrees Fahr. and drawn at 400 degrees Fahr. which is the peak of the curve of this quenching temperature is given in Fig. 23. This also is seen to be composed of martensite and darkened needles in the matrix.

The microstructure of the peak of the 1550 degrees Fahr. curve of the 1.03 per cent carbon brittle timbre steel occurring at a draw of 425 degrees Fahr. is shown in Fig. 24. The structure is martensitic, with some darkening of the needles. The coarseness of the grain is evident.

Effect of Furnace Atmosphere—Early in the course of this investigation it was found that with all conditions in regard to temperatures of quenching and drawing constant, there was a wide variation in the results obtained with certain specimens heated in the gas furnace on different days. Only specimens of the 1.03 per cent carbon brittle timbre steel behaved in this manner. However, tests of this steel quenched from a lead pot at various times were consistently uniform. Consequently it was decided to determine the effect of furnace atmospheres on the torsion impact properties. Using the data obtained by quenching from the lead pot as a base line, the effect of various gas furnace atmospheres is illustrated in Figs. 7 and 8. The average impact values based upon duplicate tests are recorded in Tables V and VI. The upper half of Fig. 7 shows clearly the relation between the 1.03 per cent carbon brittle timbre and the 1.06 per cent carbon tough timbre steels when quenched from the lead pot from 1450, 1500 and 1550 degrees Fahr.

The furnace-quenched specimens were preheated for ten minutes on the fore plate, placed in the hot zone, and uniformly heated to the quenching temperature, held for five minutes, and quenched in 15 per cent brine at 90 to 100 degrees Fahr. The total length of the treating cycle in the furnace was approximately fifteen minutes longer than that used in the lead pot. All the specimens were drawn one hour at the temperatures indicated.

The oxidizing atmosphere was one in which a wooden block when placed in the furnace immediately burst into flame, while in the neutral atmosphere the wooden block charred without burning. The reducing atmosphere was obtained by turning off nearly all of the air so that soot from the heavy hydrocarbons of the gas deposited in some portions of the muffle.

All three types of atmosphere have a marked effect on the impact values of the brittle timbre steel from quenching temperatures of both 1450 and 1500 degrees Fahr. However, at 1550 degrees Fahr. the effects are more noticeable, the poorest results being obtained in the reducing atmosphere. On the other hand the 1.06 per cent carbon tough timbre steel is little affected by any of the

Table V

Effect of Furnace Atmosphere

Torsion Impact Results on 1.06 Per Cent Carbon Tough Timbre Steel Brine-Quenched from the Gas Furnace at Indicated Temperatures, Using Various Atmospheres, and Drawn for One Hour at Temperatures Shown

Drawing Temperature Degrees Fahr.	Brine Quenched From 1450 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness	Brine Quenched From 1500 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness	Brine Quenched From 1550 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness
			Neutral Atmosphere			
275	41	66.2	..	....	..	....
325	..	....	86	65.1	..	....
350	116	63.7	..	....	..	....
375	..	....	124	63.5	48	63.4
400	..	....	..	....	114	62.4
425	69	61.9	78	61.3	..	....
450	53	60.2	..	....	..	....
475	..	....	..	....	62	59.9
			Oxidizing Atmosphere			
275	24	65.6	..	....	..	....
325	..	....	59	64.0	..	....
350	119	64.1	..	....	..	....
375	..	....	115	63.2	78	63.0
400	..	....	..	....	112	62.0
425	47	61.3	63	61.7	95	61.1
475	..	....	..	....	36	59.8
			Reducing Atmosphere			
275	67	65.5	..	....	..	....
325	..	....	69	64.6	..	....
350	116	64.7	..	....	..	....
375	..	....	124	63.4	36	63.1
400	..	....	..	....	108	62.0
425	63	61.6	70	61.1	..	....
475	..	....	..	....	57	59.8

Note: Impact values are average of at least duplicate tests and C Rockwell hardnesses are average of 20 determinations.

furnace atmospheres and produces results entirely comparable to those observed by lead pot quenching.

It is interesting to note that the peaks of both of these steels, though appreciably lower in the case of the 1.03 per cent carbon brittle timbre steel, occur at the same drawing temperature and hardness value as they did when specimens were heated in the lead pot. Incidentally it also should be noted that composite curves have been drawn for the hardness values in both Figs. 7 and 8.

For the purpose of comparison, microstructures of the 1.03 per cent carbon brittle timbre steel after brine quenching from 1450 degrees Fahr., heated in the lead pot, and in the furnace with reducing atmosphere, and drawn at 350 degrees Fahr., are given in Figs. 25 and 26. The microstructures of specimens brine-quenched from 1500 degrees Fahr., heated both in the lead pot, and in the furnace

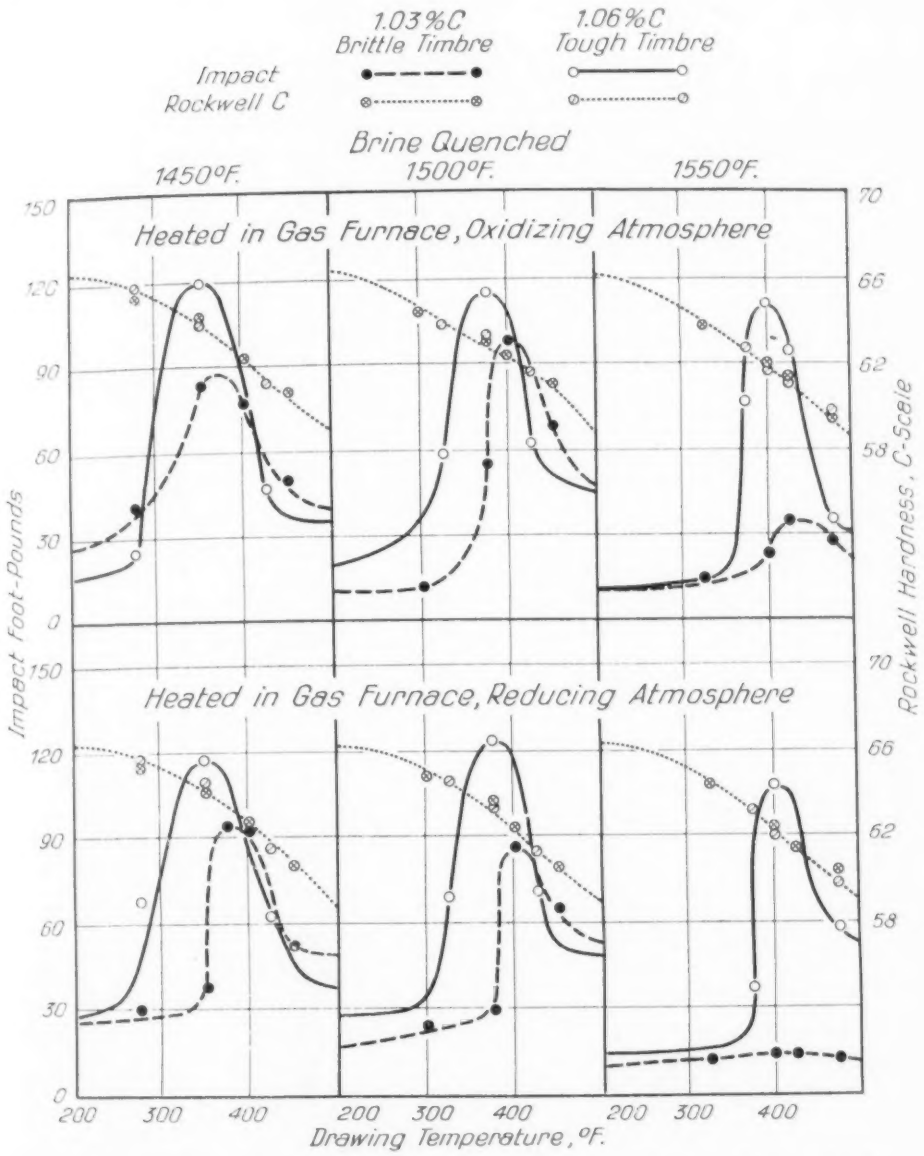

Fig. 8—Torsion Impact Results and C Rockwell Hardnesses of the 1.03 Per Cent Carbon Brittle Timbre and 1.06 Per Cent Carbon Tough Timbre Steels, Heated in the Gas Furnace with Oxidizing and Reducing Atmospheres, Brine-Quenched From the Temperatures Indicated and Drawn for One Hour at the Temperature Shown.

with reducing atmosphere, and drawn at 400 degrees Fahr., are shown in Figs. 27 and 28. The microstructures of the specimens heated both in the lead pot and in the gas furnace are identical.

The Effect of Drawing Time—The torsion impact results on the three steels included in this work, brine-quenched from the lead pot at 1450 degrees Fahr., and drawn for fifteen minutes, 1, 4, 8

Table VI

Effect of Furnace Atmosphere

Torsion Impact Results on 1.03 Per Cent Carbon Brittle Timbre Steel Brine-Quenched From the Gas Furnace at Indicated Temperatures, Using Various Atmospheres, and Drawn for One Hour at Temperatures Shown

Drawing Temperature Degrees Fahr.	Brine Quenched From 1450 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness	Brine Quenched From 1500 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness	Brine Quenched From 1550 Degrees Fahr. Torsion Impact ft.-lbs.	C Rockwell Hardness
			Neutral Atmosphere			
As quenched	13	67.0	5	66.3	5	66.8
275	19	66.0	..	....	..	....
325	..	....	17	64.7	11	64.6
350	74	64.5	..	....	..	....
375	73	62.8	49	63.5	15	63.1
400	..	....	36	62.8	..	....
425	68	61.9	44	62.2	28	61.7
475	40	59.7	22	59.7	21	60.0
			Oxidizing Atmosphere			
275	41	65.3	..	....	..	....
300	..	....	12	64.6	..	....
325	..	....	..	....	15	63.9
350	82	64.2	..	....	..	....
375	..	....	56	63.1	..	....
400	76	62.4	99	62.5	24	62.2
425	..	....	..	....	36	61.7
450	53	60.9	69	60.2	..	....
475	..	....	..	....	28	59.9
			Reducing Atmosphere			
275	30	65.3	..	....	..	....
300	..	....	24	64.8	..	....
325	..	....	..	....	10	64.4
350	38	64.3	..	....	..	....
375	95	63.2	28	63.5	..	....
400	93	62.8	86	62.3	12	62.2
425	..	....	..	....	12	61.3
450	53	60.7	65	60.2	..	....
475	..	....	..	....	10	60.4

Note: Impact values are average of at least duplicate tests and C Rockwell hardnesses are average of 20 determinations.

and 24 hours, at the temperatures indicated, are given in Table VII. Fig. 9 shows this data plotted to the same scale as previous charts. The average values used were based on duplicate tests for each quenching and drawing temperature.

The type of impact curves obtained are quite similar to those shown in previous charts, except that as the drawing time increases, the peaks move to the left. That is to say, the maximum impact value is obtained in general at a lower drawing temperature for each increase in drawing time.

The curve of the 1.06 per cent carbon tough timbre steel brine-quenched from 1450 degrees Fahr. and drawn for only 15 minutes shows a peak at 375 degrees Fahr. The 1-hour draw shows a range,

Table VII
Effect of Drawing Time
Torsion Impact—Brine-Quenched from the Lead Pot from 1450 Degrees Fahr. and Drawn at Temperatures Shown for the Length of Time Indicated

Drawing Temp. Degrees Fahr.	Drawn for 15 Min. Torsion Impact ft.-lbs.	Drawn for 15 Min. C Rockwell	Drawn for 1 Hr.	Drawn for 4 Hrs.	Drawn for 8 Hrs.	Drawn for 24 Hrs. Torsion Impact ft.-lbs.	Drawn for 24 Hrs. C Rockwell
			1.06 Per Cent Carbon Tough Timbre Steel				
212	37	67.0	47	26	62	61	66.2
275	52	66.1	60	75	92	130	65.2
325	82	65.2	112	130	116	115	64.2
350	..	.....	123	..	..	..	.....
375	129	63.6	122	123	88	60	62.4
400	..	.....	111	..	..	..	.....
425	97	61.8	70	57	57	53	60.6
			1.03 Per Cent Carbon Brittle Timbre Steel				
212	17	67.1	21	22	34	45	67.0
275	21	65.8	34	56	96	104	65.2
325	49	64.9	107	113	123	123	63.4
350	..	.....	122	..	..	..	.....
375	125	63.2	125	102	82	58	62.1
400	..	.....	110	..	..	..	.....
425	96	62.1	85	65	56	53	61.1
			0.90 Per Cent Carbon Heading Die Steel				
212	32	66.6	67	78	95	105	65.2
275	53	64.4	113	141	156	152	64.0
325	116	64.3	147	148	152	145	62.2
350	..	.....	154	..	..	..	.....
375	153	62.3	149	132	109	77	60.1
400	..	.....	130	..	..	..	.....
425	121	60.8	89	75	76	65	59.7

Note: Impact values are average of at least duplicate tests and C Rockwell hardnesses are average of 20 determinations.

with the maximum occurring at both 350 and 375 degrees Fahr. The peaks of the curves of specimens drawn for four hours and eight hours both occur at 325 degrees Fahr. After drawing specimens for twenty-four hours, the highest value was obtained at 275 degrees Fahr. It is possible that drawing in smaller increments might prevent the coinciding of peaks of series drawn at different lengths of time. The curve of the specimens of this steel drawn for twenty-four hours resembles the curves of specimens brine-quenched from 1450 degrees Fahr., shown in Fig. 5, except that the peak occurs at 275 degrees Fahr. instead of 350 degrees Fahr., and the minimum with the higher drawing temperature at 425 instead of 475 degrees Fahr.

The peaks of the curves of the 1.03 per cent carbon brittle timbre steel brine-quenched from 1450 degrees Fahr. are quite similar in that they move to the left with increasing time of draw. The maximum impact value after a fifteen minute draw is at 375 degrees

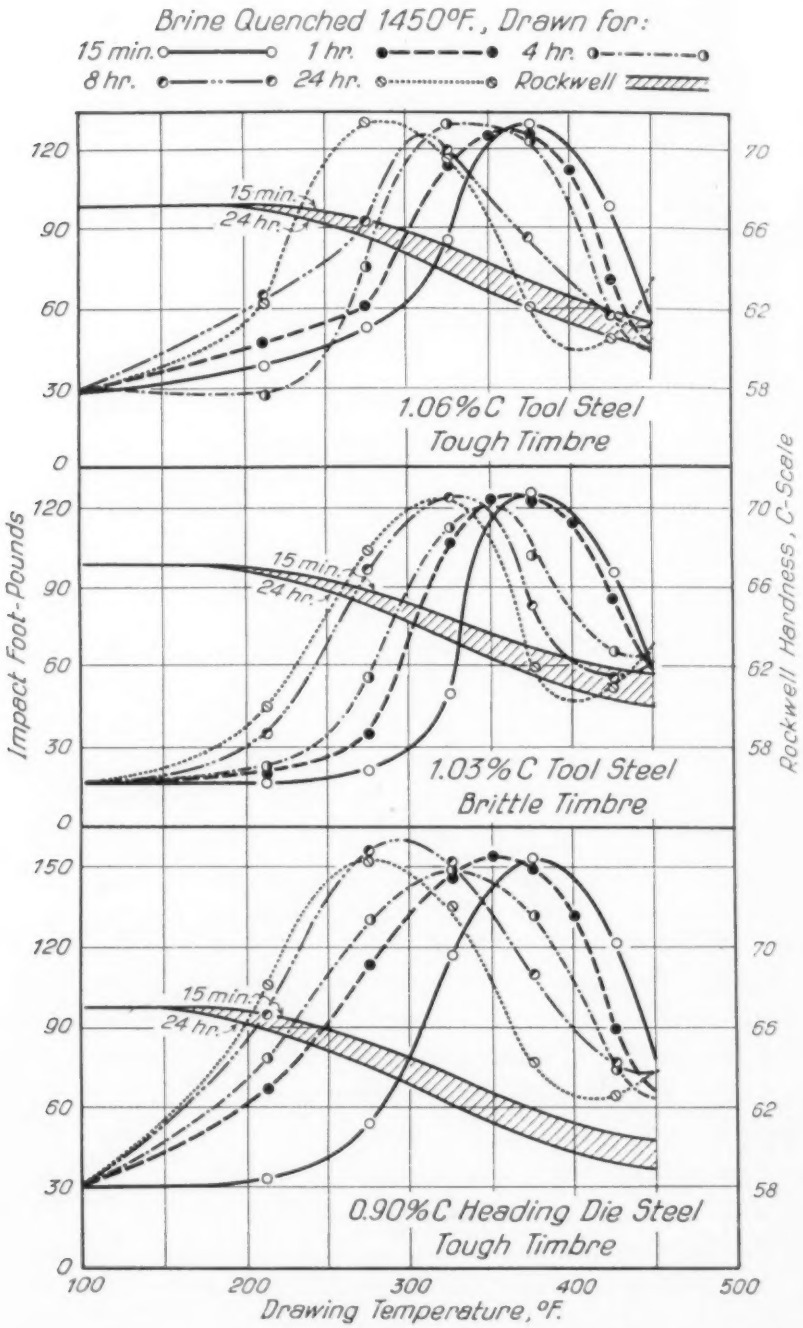

Fig. 9—Chart Showing the Effect of Drawing Time on Three Steels, Brine-Quenched from the Lead Pot from 1450 Degrees Fahr., and Drawn for the Times Indicated. The C Rockwell Hardnesses are Shown as a Range.

Fahr. After drawing for one hour, a maximum range is observed, with the highest values at 350 and 375 degrees Fahr. The peak

Table VIII
Effect of Drawing Time
Torsion Impact Results—Brine-Quenched from the Lead Pot from 1550 Degrees Fahr., and Drawn at Temperatures Shown for the Length of Time Indicated

Drawing Temp. Degrees Fahr.	Drawn for 15 Min. Torsion Impact ft.-lbs.	Drawn for 15 Min. C Rockwell	Drawn for 1 Hr.	Drawn for 4 Hrs.	Drawn for 8 Hrs. Torsion Impact ft.-lbs.	Drawn for 8 Hrs. C Rockwell
	1.06 Per Cent Carbon Tough Timbre Steel					
275	16	65.0	15	21	26	64.4
325	21	64.9	18	35	55	62.9
375	45	63.5	108	133	128	61.5
400	..	....	118	..	..	....
425	130	61.4	105	69	65	60.5
450	..	....	83	..	..	....
475	102	60.6	66	65	63	59.3
	0.90 Per Cent Carbon Heading Die Steel					
275	20	65.0	22	28	32	64.0
325	30	63.1	60	87	155	62.9
350	..	....	109	..	..	....
375	98	62.8	145	162	130	60.9
400	..	....	159	..	..	....
425	156	60.8	143	80	65	59.8
475	116	59.3	75	57	62	58.2

Note: Impact values are average of at least duplicate tests and C Rockwell hardnesses are average of 20 determinations.

of the 4-hour draw by interpolation apparently occurs at about 350 degrees Fahr. The 8 and 24-hour draws both show a maximum at 325 degrees Fahr.

The peaks of the 0.90 per cent carbon heading die steel brine-quenched from 1450 degrees Fahr., as can be seen from Fig. 9, move with more regularity to the left with increase of drawing time. The peak of the 15-minute draw occurs at 375 degrees Fahr., of the 1-hour draw at 350 degrees Fahr., and of the 4-hour draw at 325 degrees Fahr. The highest impact values of this series are obtained with the eight hour draw. The peak of this drawing time occurs at approximately 300 degrees Fahr. The peak of the 24-hour draw is at 275 degrees Fahr.

Fig. 10 shows the effect of drawing time on specimens brine-quenched from 1550 degrees Fahr., and the data is recorded in Table VIII. The curves of the 1.06 per cent carbon tough timbre steel are similar in form to the ones obtained at 1450 degrees Fahr. The peak of the 15-minute draw occurs at 425 degrees Fahr. and of the 1-hour draw at 400 degrees Fahr. The maximum impact values obtained with the 4 and 8-hour draws both occur at 375 degrees Fahr. The results of variable drawing time on the 0.90 per cent carbon heading die steel after brine quenching from 1550 degrees

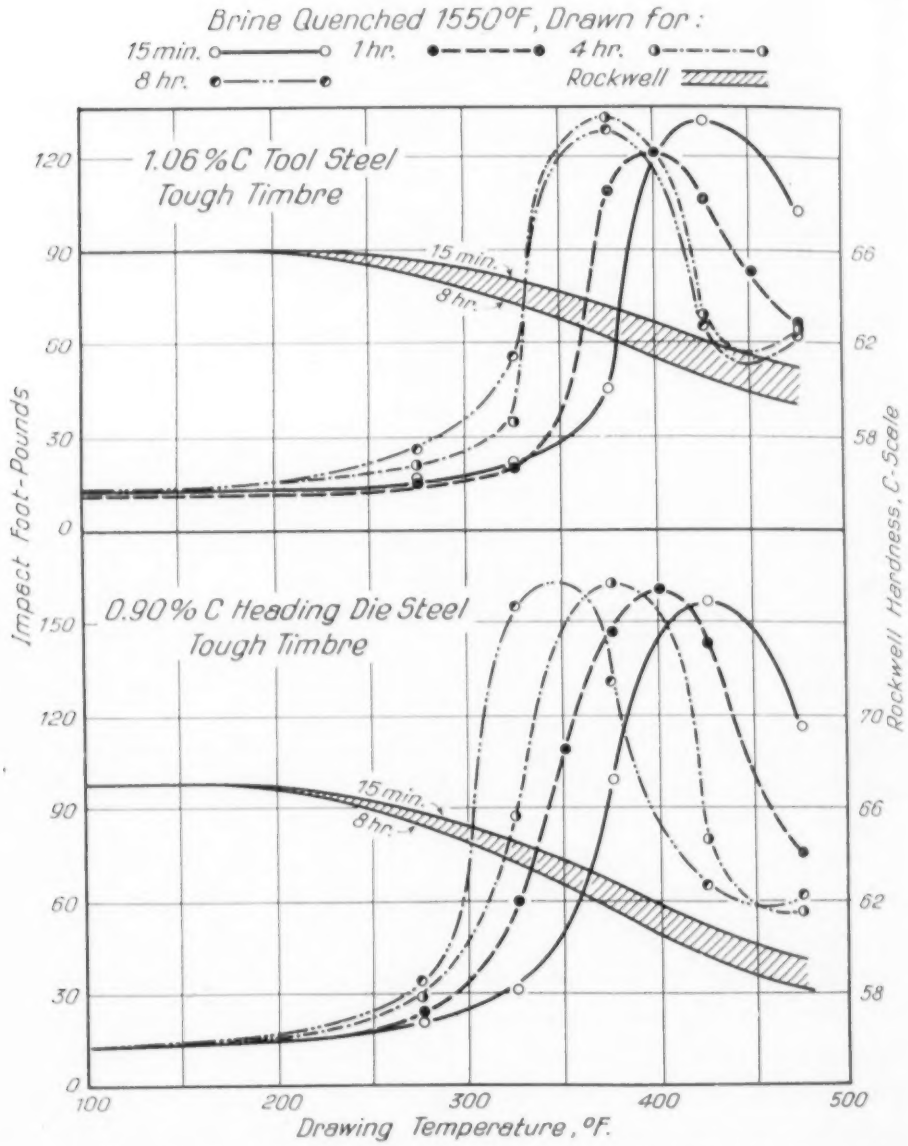

Fig. 10—Chart Showing the Effect of Drawing Time on 1.06 Per Cent Carbon Tough Timbre and 0.90 Per Cent Carbon Heading Die Steel, Brine-Quenched from the Lead Pot from 1550 Degrees Fahr., and Drawn for the Times Indicated. The C Rockwell Hardnesses are Shown as a Range.

Fahr. are also shown in Fig. 10. The peaks of the curves progress uniformly to the left with increase of drawing time. The peak of the 15-minute draw occurs at 425 degrees Fahr., decreasing 25 degrees for each period of drawing time, namely, 1, 4 and 8 hours.

Instead of drawing hardness curves in Figs. 9 and 10, the hardness range is shown. The upper limb of the cross hatched area in Fig. 9 is the curve of hardnesses taken after drawing for 15

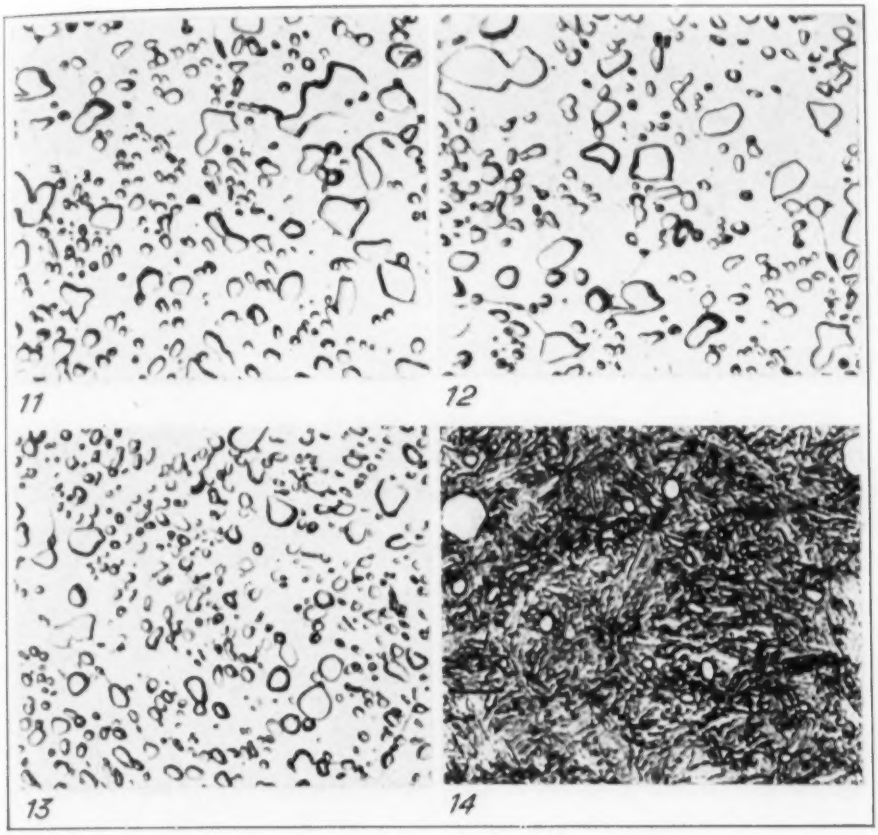

Fig. 11—Annealed Structure of 1.06 Per Cent Carbon Tough Timbre Steel.
Fig. 12—Annealed Structure of 1.03 Per Cent Carbon Brittle Timbre Steel.
Fig. 13—Annealed Structure of 0.90 Per Cent Carbon Heading Die Steel.
Fig. 14—Structure of 1.06 Per Cent Carbon Tough Timbre Steel, Brine-Quenched from the Lead Pot at 1450 Degrees Fahr., and Drawn for One Hour at 275 Degrees Fahr. All Specimens Etched for 5 Seconds in 2 Per Cent HNO_3 in Alcohol. × 1000 Excepting Fig. 14—× 1500.

minutes, and the lower limb after drawing for 24 hours. The same is true of Fig. 10, except that the lower limb is the hardness curve of specimens drawn for 8 hours. The difference between the 15-minute and the 24-hour draw is not more than two points Rockwell.

Attention is drawn to the fact that there is very little difference in the magnitude of the impact values after various lengths of draw. There is only a slight tendency for the impact values to be higher with longer drawing time. Incidentally the actual values of the peaks are very similar to those shown in Fig. 5.

The curves of the specimens brine-quenched from 1550 degrees Fahr., shown in Fig. 10, are seen to be moved to the right as was indicated in Fig. 5. For instance, the peak of the series of the 0.90 per cent carbon heading die steel brine-quenched from 1550 degrees

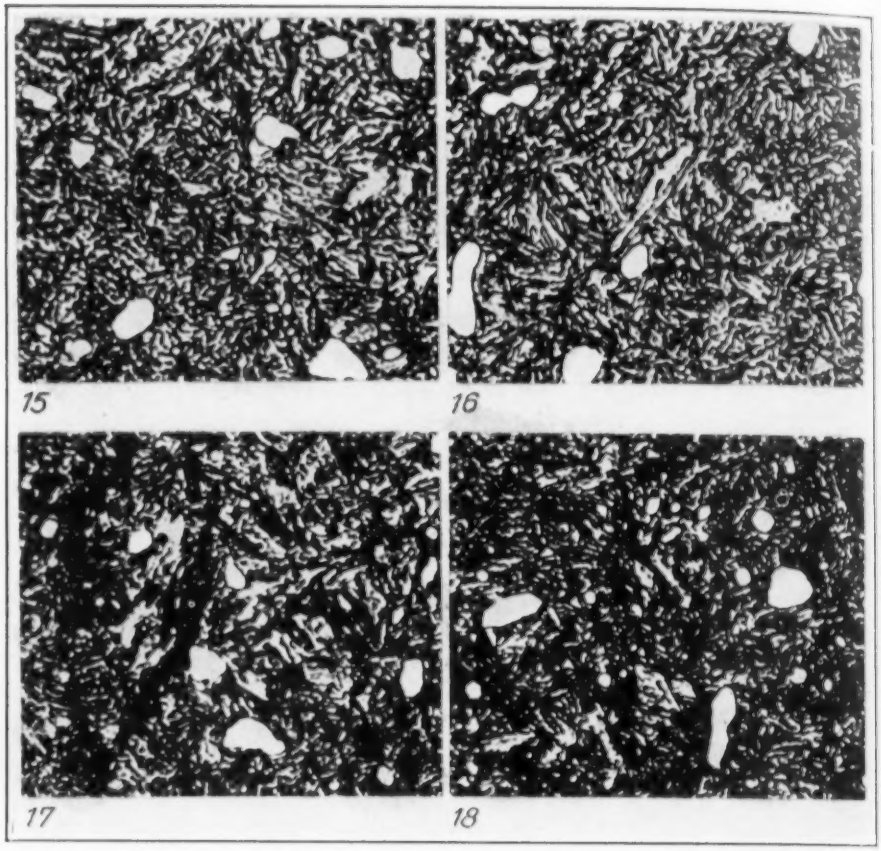

Fig. 15—Structure of 1.06 Per Cent Carbon Tough Timbre Steel Brine-Quenched from the Lead Pot from 1450 Degrees Fahr. and Drawn for One Hour at 325 Degrees Fahr.

Fig. 16—Same, Drawn at 350 Degrees Fahr.

Fig. 17—Same, Drawn at 375 Degrees Fahr.

Fig. 18—Drawn at 400 Degrees Fahr. All Specimens Etched for 5 Seconds in 2 Per Cent HNO_3 in Alcohol. × 1500.

Fahr. and drawn for 8 hours is at 350 degrees Fahr., while the peak of this steel as brine-quenched from 1450 degrees Fahr. and drawn for 8 hours is at 300 degrees Fahr.

The microstructures of the 1.06 per cent carbon tough timbre steel brine-quenched from 1450 degrees Fahr. and drawn at 325 degrees Fahr. for various times are as follows:

15 minutes	Martensite	(Similar to Fig. 14)
1 hour	Martensite	(Similar to Fig. 15)
4 hours	Martensite with some darkening of the needles	(Similar to Fig. 16)
8 hours	Martensite and a large number of the needles in the matrix darkened	(Similar to Fig. 17)
24 hours	Martensite with increasing numbers of the needles darkened	(Similar to Fig. 17)

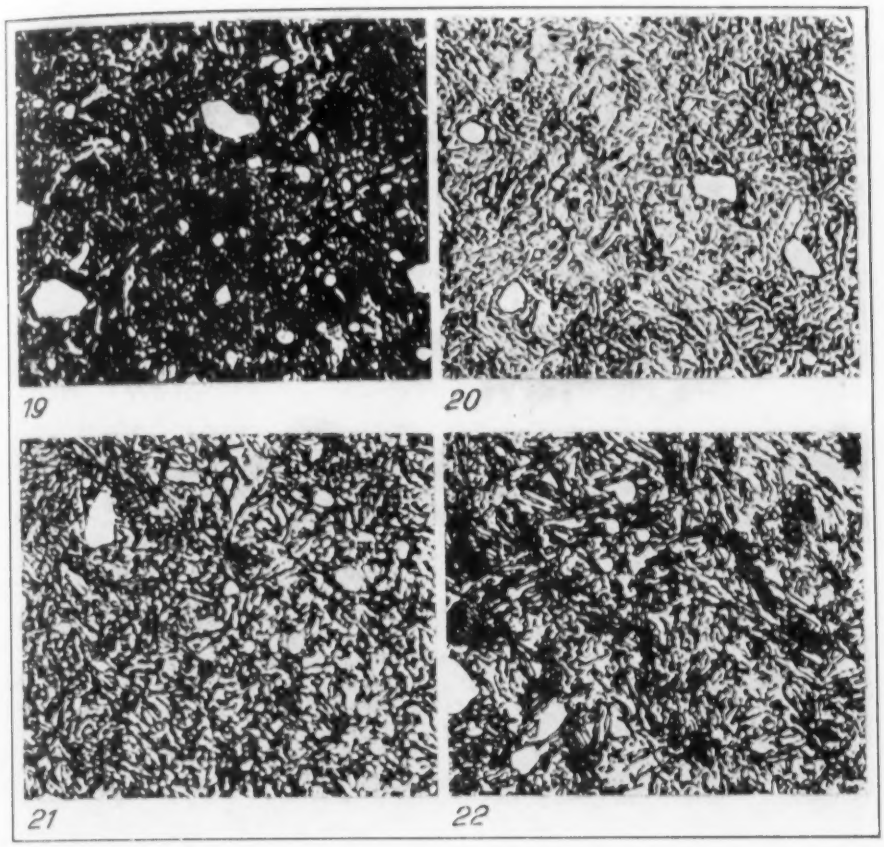

Fig. 19—Microstructure of Specimens of 1.06 Per Cent Carbon Tough Timbre Steel, Brine-Quenched from the Lead Pot, and Drawn for 1 Hour at Temperatures Indicated. Brine-Quenched from 1450 Degrees Fahr., and Drawn at 425 Degrees Fahr.

Fig. 20—Same, Brine-Quenched from 1500 Degrees Fahr., and Drawn at 275 Degrees Fahr.

Fig. 21—Same, Brine-Quenched from 1500 Degrees Fahr., and Drawn at 325 Degrees Fahr.

Fig. 22—Same, Brine-Quenched from 1500 Degrees Fahr., and Drawn at 375 Degrees Fahr. All Specimens Etched for 5 Seconds in 2 Per Cent HNO_3 in Alcohol. × 1500.

Discussion of Results

The torsion impact test shows that there is a state of maximum toughness in quenched and slightly tempered carbon tool steel. The impact values rise with increase of drawing temperature to a peak at a certain temperature. The position of the peaks depends upon the material in question, the temperature of quench and time of draw. The rapid rise in impact strength with low drawing temperatures is undoubtedly partially due to relief of residual stresses. As quenched the values are low, since the alpha iron is supersaturated with carbon and in a highly strained condition. The atomic agitation

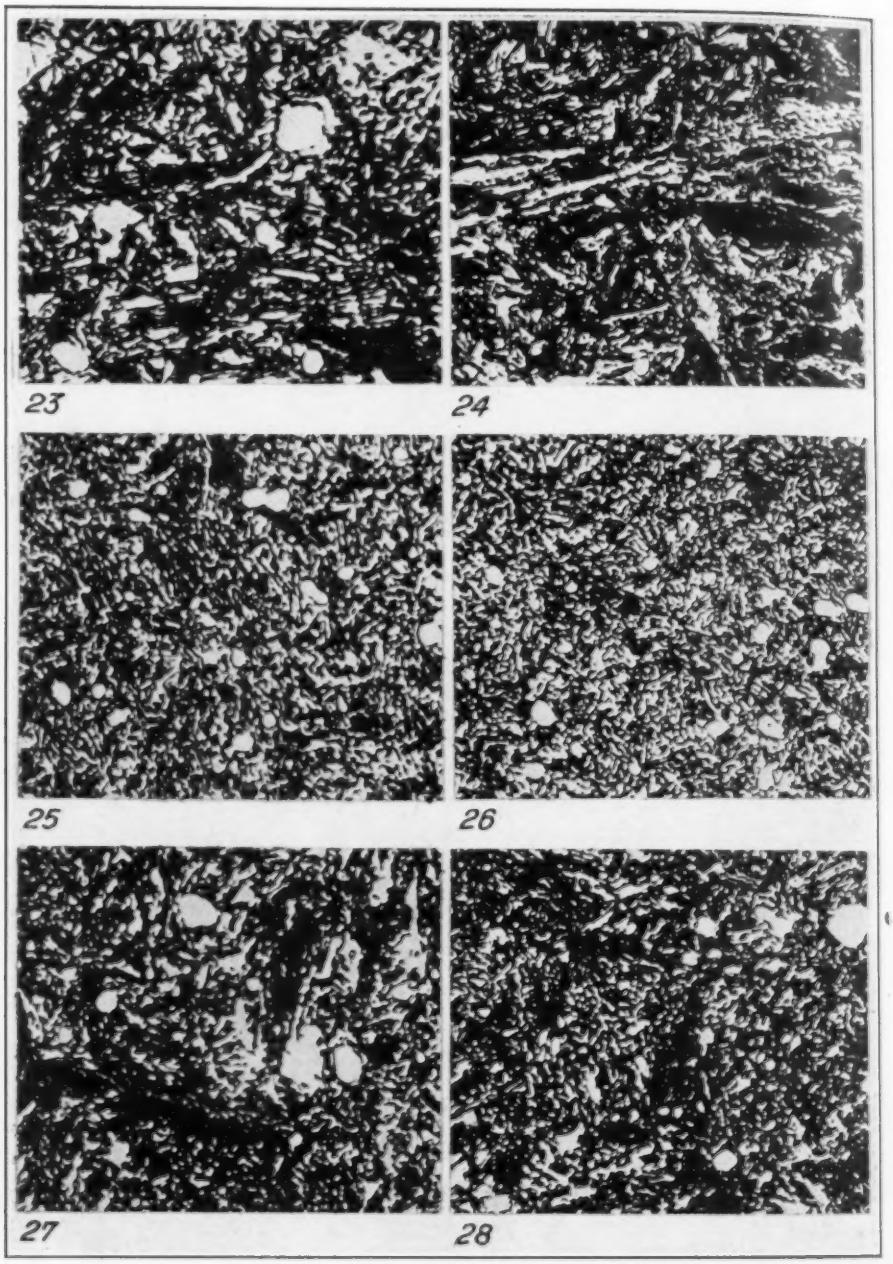

Fig. 23—1.06 Per Cent Carbon Tough Timbre Steel, Brine-Quenched from Lead Pot at 1550 Degrees Fahr., Drawn One Hour at 400 Degrees Fahr.

Fig. 24—1.03 Per Cent Carbon Brittle Timbre Steel, Brine-Quenched from Lead Pot at 1550 Degrees Fahr., Drawn One Hour at 425 Degrees Fahr.

Fig. 25—1.03 Per Cent Carbon Brittle Timbre Steel, Brine-Quenched from Lead Pot at 1450 Degrees Fahr., Drawn One Hour at 400 Degrees Fahr.

Fig. 26—Microstructure of 1.03 Per Cent Carbon Brittle Timbre Steel, Heated in the Furnace with Reducing Atmosphere, Brine-Quenched from 1450 Degrees Fahr., and Drawn for One Hour at 400 Degrees Fahr.

Fig. 27—1.03 Per Cent Carbon Brittle Timbre Steel, Brine-Quenched from 1500 Degrees Fahr., Drawn One Hour at 400 Degrees Fahr. in Lead Pot.

Fig. 28—Same, Heated in Gas Furnace with Reducing Atmosphere. All Specimens Etched for 5 Seconds in 2 Per Cent HNO_3 in Alcohol. × 1500.

due to tempering at a low temperature results in a slight agglomeration which not only relieves strain but increases ductility.

Tempering at peak temperatures unquestionably represents a fairly complete removal of internal strains. Peak temperatures correspond to the point at which the retained austenite starts to transform. Scott[10] shows this clearly by volume and size change determinations.

Drawing at temperatures beyond the peak rapidly lowers the impact strength. This phenomenon is possibly due to the fact that the cementite and ferrite is approaching or has passed a certain critical size which weakens the structure. Perhaps a more important reason for this condition is the low ductility of the mixed structure resulting from the transformation of the retained austenite. At least the low points of the impact curves after passing the peaks, occur at drawing temperatures corresponding to the maximum increase in length due to the full conversion of all of the retained austenite. After this point is passed, the impact strengths recover gradually.

Following this reasoning, the movement of the peaks to higher drawing temperatures, as the quenching temperatures increase, is probably due to two factors. Higher quenching temperatures have been shown to increase the amount of retained austenite[11] and the residual stresses [12]. Consequently higher drawing temperatures are needed to reduce the stress proportionately. Austenite begins to transform at the peaks and the impact values drop similarly to the phenomenon encountered with lower quenching temperatures.

This is further substantiated by the fact that increasing the drawing time for any given quenching temperature moves the peaks to the left. The longer drawing times offer more opportunity for stress relief at a given temperature.

The lower impact values of the brittle timbre steel are probably due to the effect of the increase in grain size on the plasticity, and consequently the toughness. The results obtained with the brittle timbre steel correspond to those obtained with the tough timbre types

[10]Howard Scott, "Dimensional Changes Accompanying the Phenomena of Tempering and Aging Tool Steels," TRANSACTIONS, American Society for Steel Treating, Vol. IX, February, 1926, p. 277.

[11]Loc. cit.

[12]O. V. Greene, "Estimation of Internal Stresses in Quenched Hollow Cylinders of Carbon Tool Steel," TRANSACTIONS, American Society for Steel Treating, Vol. 18, 1930, p. 369.

after still higher quenching temperatures. That is, if the foregoing theory is correct, the brittle timbre steel was in a more highly stressed condition, since the peaks are about 25 degrees Fahr. higher for each quenching temperature as compared to the tough timbre steels.

The effect of furnace atmosphere on the brittle timbre steel may be explained by the rate of heating in the furnace as compared to the rate of heating in the lead pot. The rate of heating in the lead pot was considerably more rapid and did not allow as much grain growth in the brittle timbre steel. This seems to be substantiated by the fact that the curves of the tough timbre and brittle timbre steels shown in the upper left hand section of Fig. 7 can be made to separate by holding for extended periods of time in the lead pot before quenching.

Summary and Conclusions

The data recorded in this investigation throw considerable light on the phenomena occurring during the hardening and tempering of carbon tool steel. A quantitative evaluation of certain mechanical and metallurgical properties of these steels when tested under conditions of dynamic loading has been shown. A summary of these characteristics is as follows:

1. The correct drawing temperature for maximum toughness increases with increase of quenching temperature and decreases with increase of drawing time. While both under-drawing and over-drawing in respect to time and temperature decrease the impact value, the range for approximately maximum toughness usually extends over a range of 50 degrees Fahr.

2. There is a considerable difference in the toughness of steel of the same analysis, but of different timbre, and also a noticeable difference in steels of differing carbon contents. Brittle timbre steels not only have lower impact values when quenched by the usual methods, but have the peaks of maximum impact at higher drawing temperatures than tough timbre steels of the same analysis. Lower carbon increases the toughness, and shows no decrease in impact value as the quenching temperatures are raised within the range reported.

3. The effect of various furnace atmospheres on the toughness of brittle timbre steels is very marked, while tough timbre steels

are but little affected. Incidentally the peaks of maximum impact value are not displaced laterally by various heating media.

4. Increase of drawing time does not increase the impact value as might be expected, but merely moves the peaks to a lower drawing temperature. In a number of cases the eight and twenty-four hour draws coincided, showing that a certain temperature was necessary for stress relief irrespective of time. The peaks for the specimens quenched at higher temperatures and drawn for different lengths of time are moved farther to the right than those for the same steel quenched at a lower temperature and drawn for a similar length of time.

5. It has been suggested that the peak of maximum toughness in drawing carbon tool steel is due to a fairly complete removal of residual stress and a slight agglomeration of the submicroscopic cementite and ferrite. The drop of impact value with hardness beyond the peaks, as drawing progresses, is thought to be due essentially to the mixed structures resulting from the transformation of the retained austenite. Accompanying this condition there is also the possible weakening of the structure due to a critical size of the cementite and ferrite in the original martensite.

In conclusion, a word of caution in the interpretation of these results might not be amiss. It should be remembered that the test section of the specimens used is only ¼ inch in diameter and therefore allowances should be made for the size of actual tools, particularly when time of drawing is to be considered. However the trend of this variable on carbon tool steel is unquestionably established. It might be convenient to regard variables such as impact, drawing temperature and drawing time for given quenching temperatures as dimensions of a solid figure. A similar solid figure might be constructed by maintaining a constant drawing time and using quenching temperature as the third variable. From this point of view the charts shown in this paper could then be considered as merely planes through one of these solid figures. There are many other conditions such as analysis, original structure, time of heating cycle, heating and quenching media, and size, which should be kept constant in order to correctly evaluate the torsion impact properties of a steel. Sufficient work has been done in regard to some of these variables to show that they very definitely affect the torsion impact properties of a steel, and it is hoped that the results of this work may be presented in the near future.

DISCUSSION

Written Discussion: By John F. Wyzalek, Hyatt Bearings Division, General Motors Corp., Newark, N. J.

The authors are to be congratulated upon the ingenious and practical methods developed to determine impact values in steels having a high degree of hardness and low ductility.

The method appears to offer a quick and reliable means of determining the correct treatment for steels of high hardness which must withstand severe service. The correlation of the value as derived through same with actual performance records of steels as applied to production tools will prove unquestionably of appreciable value. It will be interesting to see what this method of impact testing will develop in steels with variations in test conditions as indicated by the authors.

May it be suggested that they also consider the effect of surface conditions of the steel as influenced by furnace atmospheres or by mechanical means such as grinding, lapping, burnishing or polishing.

Extension of tests to develop the value of this method of impact testing should be encouraged, and the presentation of results of same will be unquestionably looked forward to with considerable anticipation.

Written Discussion: By Robert S. Rose, metallurgical department, Vanadium Alloys Steel Co., Latrobe, Pa.

The determination of impact properties of hardened and drawn carbon tool steels is of considerable technical and practical importance. During the past two years we have been fortunate in having somewhat similar determinations of high speed and many alloy steels, but, strangely enough, carbon steels which find the greatest use and widest application have been somewhat neglected. It is, therefore, extremely pleasant to welcome this significant paper of Luerssen and Greene.

It is presumed that in all cases the ¼-inch test specimens were hardened throughout their entire cross section. This obviously precluded the determination of results based upon the usual composite structural condition of carbon steels. Perhaps, if it were possible to test specimens of larger diameter, the effect of various depths of penetration would be found significant.

It is somewhat regretted that the authors have found it necessary to continue the use of such confusing terminology as "timbre." At least, it is believed that since the term is directly applicable to a specific property of the steel, it is also capable of complete identification. There is every reason to believe that "timbre" as used by the authors simply represents the susceptibility to grain growth at temperatures sufficiently high to provide adequate atomic mobility. "Brittle timbre" and "tough timbre" do not seem to present a true picture of the relative toughness of the two steels. As a matter of fact when quenched from 1450 degrees Fahr. the data show 125 foot-pounds at the peak for the brittle timbre steel and 123 foot-pounds at the peak for the tough timbre steel. The authors thus establish that when these two steels have comparable grain size, their toughness properties are practically identical. The fact that the brittle timbre steel shows appreciable reduction in impact value compared with the tough timbre at higher quenching temperature is therefore not an inherent

or primary deficiency such as brittle timbre would imply, but apparently due to a secondary cause, larger grain size, since this steel is more susceptible to grain growth.

Depth of hardening has been mentioned by the authors as the one other characteristic difference, but Bain has given indisputable proof that coarse grain promotes deep hardening by reducing the reaction rate of phase transformation and Dehlinger's hypothesis of slower lattice changes (inner-atomic) in coarse grain material to a great extent accounts for this phenomenon. It consequently follows that since depth of hardening is a function (within limits) of grain size and since at low quenching temperature both steels show similar plasticity, brittle timbre and tough timbre are confusing if not actually erroneous terms. It would appear that a more correct and specific discrimination could be made by their grain-growing tendencies.

The authors' explanation for the trend of the impact curve is in general agreement with our own views and those of other investigators. However, we are inclined to lay less emphasis on the effect of residual strain at temperatures above about 275 to 300 degrees Fahr. Ohman has given more than sufficient proof from lattice dimension determinations that the alpha martensite of quenched carbon steel is decomposed into cementite and ferrite when tempered at 300 degrees Fahr. Since the specific volume of cementite and ferrite is less than that of alpha martensite, it seems reasonable to assume that all internal strain of enforced solid solution has been relieved when this temperature has been reached.

It then becomes necessary to explain the peak toughness as essentially due to the aggregation of all the molecularly or colloidally dispersed carbide to greater than a certain minimum size. Whether the effect on plasticity of the particle size of precipitated carbide is entirely mechanical or due to some energy change is not known. Since the strain of the volume expansion of austenite to cementite and ferrite is credited with being responsible for the major part of the low plasticity following the maximum toughness, we would like to know whether any determinations were made enabling an estimation of the percentage of austenite retained.

The data obtained from various drawing periods while not unexpected are interesting and serve as additional evidence invalidating a popular belief that some mysterious beneficial effect results only from prolonged drawing. It is evident that the same reactions occur at all drawing temperatures since none of the phases present are stable, only the speed of the reaction being a function of temperature.

A paper of this kind entails considerable experimental difficulties in minimizing the number of variables which would seriously distort the results obtained. It is therefore my desire to commend the authors for the thorough and systematic manner in which these data have been presented.

Written Discussion: By S. C. Spalding, assistant metallurgist, American Brass Co., Waterbury, Conn.

The paper on impact properties of tool steel is a very interesting one though we cannot agree with the conclusions drawn from the data that 350 to 375 degrees Fahr. is the drawing point of maximum toughness of hardened carbon tool steel. Looking at the data as set down we find that tool steel

hardened in brine and drawn at 350 to 375 degrees Fahr. is much tougher in impact than the same steel hardened and drawn at 800 degrees Fahr. To anyone who has ever made and hardened tools or worked with tool steel this is hard to believe. The following simple experiment will readily demonstrate this. Quench two samples of tool steel in brine at 1450 degrees Fahr. Draw one at 350 degrees Fahr. and one at 800 degrees Fahr. Place each in a vise and break with a hammer. The one with 350 degrees Fahr. draw will snap readily while the one with 800 degrees Fahr. draw will break with difficulty and bend before breaking. From a structural standpoint the structure at 375 degrees Fahr. draw is mainly martensitic, after 800 degrees Fahr. draw sorbitic. Could we then argue that martensite is tougher than sorbite? To look at it in a different way I venture to say that any of us who have made tools and had them break when hardened and drawn at say 350 degrees Fahr. have cured the trouble by drawing at 400 or 450 degrees Fahr. or higher, yet were we to believe the evidence of this paper these higher draws made them less tough. Before the advent of alloy spring steels many springs flat or coiled were made of a carbon steel of approximately tool steel analysis. It is common knowledge that these springs if drawn at 350 degrees Fahr. would be brittle and break, whereas for proper spring properties 600 to 800 degrees Fahr. draw was required. A coiled spring when stressed is in torsion, so here again we seem to have contradictory evidence from practice. From the very evident failure of the data from the torsion impact test to line up with conditions of actual practice with tools or tool steel we conclude that the data indicate rather some local conditions of strain relief peculiar to the actual test piece and test method than the property of impact toughness of tool steel.

Written Discussion: By J. V. Emmons, metallurgist, Cleveland Twist Drill Co., Cleveland.

The development of the torsion impact test by Luerssen and Greene and its utilization in studying the properties of hardened tool steel is most interesting. The writer has been particularly interested because of his long established opinion that future improvements in the manufacture and utilization of tool steel may depend to a large extent upon a better understanding of its physical properties. The torsion impact test is believed to be a useful addition to our limited means of accurately measuring some of these physical properties.

The results obtained by the authors upon carbon tool steels have been compared with those obtained upon a similar steel by R. L. Sanford and the writer[1] using a static torsion test method. It is observed that the authors' curves for "impact in foot-pounds" at varying tempering temperatures, bear a strong resemblance to those obtained by Mr. Sanford and the writer for plastic deformation at varying tempering temperatures. Both methods agree that there is a definite maximum in the curve at a tempering temperature about 400 degrees Fahr. and an equally definite minimum at about 500 degrees Fahr. Such agreement by the two different methods increases our confidence in the accuracy of both.

It is believed that the results obtained by the static torsion method are more complete than those obtained by the torsion impact method. To be specific,

[1]*Proceedings*, American Society for Testing Materials, Vol. 32, Part II, 1932, p. 380.

the static method gives direct values for ultimate torque and ultimate deformation as well as stress-strain curves from which values for the plastic deformation, the proportional limit and the modulus of elasticity may be taken.

The authors' results upon the effect of furnace atmospheres and tempering times, are particularly interesting and deserving of careful consideration.

The authors make extensive use of the terms "brittle timbre" and "tough timbre" but the exact meaning is not clear. It would be appreciated if they would give us definitions and explain how they determine whether the "timbre" of a steel is tough or brittle.

The authors are to be congratulated upon their work and it is hoped that their promise of additional reports of results will soon be fulfilled.

Written Discussion: By John H. Hall, Taylor-Wharton Iron and Steel Co., High Bridge, New Jersey.

I have not had time to digest thoroughly the interesting and important paper by Luerssen and Greene, but I cannot refrain from expressing my admiration for the ingenuity of the test method they have devised. I believe that their work represents a real step forward in the detection of variations in the toughness of our hard metals, and that it will be of very great value in the future to those making and using such materials. In particular, the precision with which the differences in shock toughness between brittle timbre and tough timbre steels is brought out, is most interesting and striking.

On page 314 the photograph in Fig. 3 does not seem to agree exactly with the sketch in Fig. 2. As I read the pictures the cross piece marked "h" in Fig. 2 is omitted in the photograph.

On page 315, second paragraph, in the description of the operation of the machine, it is not quite clear whether the friction wheel, which drives the flywheel "c", is disengaged from the flywheel after the apparatus is brought up to speed and before breaking the specimen. I take it, however, that this is the method of testing employed, as otherwise it would not be possible to ascertain the residual speed.

It is interesting to note that in all the steels, as shown on pages 318 and 319, it is necessary to use progressively higher drawing temperatures in order to secure maximum toughness as the quenching temperatures are raised. The explanation given for this on page 335 is no doubt the correct one. The extraordinary decrease in the maximum toughness secured in the brittle timbre steels at higher quenching temperatures is most striking, and particularly so by contrast with the behavior of the tough timbre steels.

In the second paragraph on page 320—last line, the fact that, in the 0.90 per cent carbon tool steel, the maximum shock toughness secured rises slightly as the quenching temperature is increased is a little difficult to explain, especially as it is in contrast to the behavior of the tough timbre steel of slightly higher carbon.

The data set forth on pages 323 and 324, showing the effect of furnace atmosphere on the toughness of the brittle timbre steel, are also very striking. The explanation of this, given in the second paragraph on page 336, i.e., that it is due to greater grain growth, resulting from the slower heating in the furnace, is no doubt correct, but this does not seem to be the entire explanation, as it is not immediately clear why the reducing atmosphere should give the poorest

results. Are we to infer that the reducing atmosphere corresponded to the slowest heating in the furnace, and the oxidizing atmosphere to the fastest heating?

The fact brought out on page 326 that with greater drawing time the maximum toughness is secured at lower drawing temperatures is what one would expect, but it is surprising that there is no increase in the amount of shock strength. One would have expected at least a slight increase in the shock figure, as the drawing time was increased and the hardness decreased.

In Table VIII and Fig. 10 I note that the brittle timbre tool steel has been omitted. As the brittle timbre steel had greatly decreased shock strength on quenching from 1550 degrees Fahr., it would be interesting to know the effect of increasing the drawing time after quenching this steel from 1550 degrees Fahr. In particular, one is moved to wonder whether, in this case, there is an increase in shock strength with increased drawing time, rather than simply a lowering of the temperature at which maximum toughness is secured.

It is interesting also to note that with longer drawing times it is still true that higher drawing temperatures are required for maximum toughness when the quenching temperature is increased.

One of the most striking facts brought out is that, in order to secure maximum shock strength, the drawing temperature must be closely controlled in all steels.

I regret that I have not had time to read this paper with the more careful attention it deserves, and that I cannot be present to take part in the discussion.

A. H. D'ARCAMBAL:[2] In merely sketching this excellent paper one might be led to believe that practically all carbon steel tools should be drawn in the neighborhood of 350 degrees Fahr. for maximum life. Service tests have definitely proven, however, that certain types of tools, such as taps, reamers, etc., must be drawn from temperatures in the neighborhood of 450 to 500 degrees Fahr., where maximum resistance to breakage is desired. We must consider of course that a tool such as a tap with the cutaway section has entirely different strains setup when brine-quenched than does a simple plain round test piece. Also, the rate of heating is a very important factor that would result in some differences in physical properties, should you be able to measure torsional impact of finished metal cutting tools.

The authors have brought out a very important point in regard to the desirability of heating carbon steel cutting tools in a lead bath (undoubtedly just as good results in a salt bath) rather than in a box type furnace or open fire method. It is the general practice of practically all metal cutting tool manufacturers to heat these carbon tools in the lead bath or salt bath, rather than employing the open fire, with the possible exception of tools such as milling cutters.

I know that we are all going to obtain a great deal of value from this paper, and trust the authors will continue with their splendid work.

A. V. DE FOREST:[3] This type of equipment is of importance in giving a picture of the fact which is too often overlooked—that brittleness and hardness

[2]Consulting metallurgist, Pratt & Whitney Co., Hartford, Conn.

[3]Consulting metallurgist, 929 Connecticut Ave., Bridgeport, Conn.

are not necessarily coupled together by a rigid draw box. Under certain conditions toughness can be increased without sacrificing hardness, as the peaks in this peculiar looking curve certainly prove. There is some form of toughness which is independent of hardness, and as we get that idea in mind, it is going to improve the question of the heat treated steels, perhaps beyond anything that we have at present.

H. G. KESHIAN:[4] Among the many practical questions which this interesting paper brings out there is one to which I would like to call attention: namely, the effect of the length of drawing time on the impact properties of hardened tool steel.

Some heat treaters when drawing a hardened tool aim to simply "take the snap off the tool" by either warming the tool in front of a furnace, or leaving it in hot water, or by drawing it to color. Others, of more searching type of mind, are anxious to know the most effective length of drawing time for maximum toughness.

There are some who claim, for instance, that a certain tool should be drawn at a given temperature, say for one hour, and others claim that it should be drawn three hours. There are still others who believe that the longer the tool is drawn the tougher it will be.

I just recently heard of one of our esteemed speakers on heat treating as having said in one of the Chapter meetings that when he was visiting one of the heat treating departments of a European plant he asked the heat treater how long he was going to temper the tool which he had just quenched and put into the drawing furnace. He was very much delighted to get an answer that the visitor had long desired to hear in this country which was to the effect that, the hardener was going to draw the tool for thirty-five hours. Whereupon the visitor said to himself "Thank Heaven, here I have found at least one man who was going to draw a tool the way it should be."

I hope that I got the story right, and if not, I still will be within striking distance of the truth if I say that there are many people among the heat treaters, or among those who tell the heat treaters how to heat treat, who strongly advocate that a tool must be drawn as long a time as possible; in other words, as long as the heat treating department can hold back the demand of the production department for tools.

In order to explain this difference of opinion on such a practical phase of heat treating, there is no need to go to the extreme view of explaining it as a sinister desire on the part of heat treating equipment manufacturers to incite greater demand for more tempering furnaces, neither need we explain this recommendation of long time draw as a method of safe play on the part of those who have to do with the selection or recommendation of steel for tools.

There seems to be two main reasons for this difference of opinion. First, the lack of sufficient practical data for those who claim this atrociously long draw. Second, the lack of realization, on the part of these people, of what an excessively long draw would mean to a heat treating department both in the way of waste of time and money and additional equipment. Particularly is this true in a heat treating department handling a great variety of tools which cannot be handled on purely straight line production basis.

[4]Metallurgist, Chase Co., Inc., Waterbury, Conn.

It is worthy of note that the authors found "very little difference in the magnitude of the impact values after various lengths of draw" as stated on page 331 and shown in Fig. 10. The difference of impact properties of specimens drawn for fifteen minutes and eight hours is quite negligible.

In the application of this fact the type of steel and the section of the tool must, of course, be considered: but as a whole the results of the authors agree quite well with my experience, and I am sure with the experience of many other observers that, from the standpoint of production nothing is gained by tempering a hardened tool beyond a certain length of time, and on the contrary, like many other exaggerations it will lead only to waste and confusion.

Authors' Closure

Both Mr. d'Arcambal and Mr. Keshian have mentioned important points in their remarks. Mr. d'Arcambal to a certain extent answered his own objection when he said that treating conditions have an important effect on the service of tools. It is necessary to keep in mind that our data are fundamental and can only be applied to actual practice with care. We are entirely in agreement with Mr. d'Arcambal that a tool, such as a tap in which a compromise between hardness, toughness and cutting efficiency must be obtained, cannot always be directly compared with an ideal section such as that used for torsion impact specimens. A word of caution in this respect is given in the conclusion of the paper.

Mr. Keshian's remarks in regard to drawing temperatures used in actual practice for the treatment of various tools should be of interest to both Mr. Wyzalek and Mr. d'Arcambal. However, Mr. Wyzalek is entirely justified in his remarks in regard to the correlation of information obtained by the torsion impact machine and actual performance records. We have some definite indications that under a given set of conditions, peak values produce the best results in actual service.

We have done some work in regard to the finish on specimens. However the work was not done on carbon tool steel, which is covered in this paper, but on high speed steel. A number of specimens were polished after hardening, some were left in the scaled condition, some were sand blasted, and a few were left in the rough machined condition. The polished, the scaled and the sand blasted specimens all had approximately the same results. The impact values were between 74 and 77 foot-pounds. The specimens tested in the rough machined condition showed an impact value of only about 50 foot-pounds. These specimens had all been oil-treated from 2350 degrees Fahr., and drawn for one hour at 1050 degrees Fahr. All of the carbon steel specimens in this paper were machined 0.001 or 0.002-inch oversize, treated from the lead pot, and then polished with 000 French emery by hand.

The remarks made by Mr. Spalding seem to relate to characteristics of ductility. It should be pointed out that the torsion impact machine is giving information in regard to impact resistance. It is hardly correct to consider these as similar properties. No application of the machine has yet been made on problems relating to steels drawn in the hardness range referred to by Mr. Spalding. However it is interesting to note that the torsion impact curve rises when those structures are reached.

Mr. Spalding's discussion brings the important question of whether a tool will be satisfactory if it bends before it breaks in impact or whether a tool is more desirable if it is strong enough so that it will not break at all under similar conditions of loading. That is to say, the same amount of impact energy under certain conditions that would bend or put a permanent set in a tool drawn in the higher temperature range probably would have no effect at all on a tool drawn in the peak range. The physical properties that are determined by the torsion impact test are quite likely the resultant of two characteristics. As the toughness increases in drawing, the hardness (or tensile strength) decreases, and the impact value does not recover sufficiently until a high degree of toughness is obtained to offset the decrease in hardness.

Mr. Rose regrets our use of the terminology of "timbre," but we doubt that the average steel treater will have any more difficulty in understanding this term than such nomenclatures as "phase transformations" or "lattice changes." Referring to the discussion of both Mr. Rose and Mr. Emmons, the term "timbre" is a very convenient general term to describe differences in behavior upon heat treatment, which cannot be accounted for by analysis alone. These differences may have to do with grain size, impact resistance, penetration, susceptibility to furnace atmosphere, etc. In the present case we are interested in the inherent properties affecting impact resistance, and consequently for the sake of simplicity, steels of certain inherent characteristics are freely referred to in the paper as tough or brittle timbre. While the factors that influence the inherent characteristics of a heat such as grain size and hardenability may be considered as secondary, they are of just as much significance as those called primary. The primary factors are usually reserved in our present terminology to refer to the effect of elements in solid solution in the austenite. The brittle timbre steel used in this work was of a type that invariably showed the minute cracks described by Lucas and Bain. While this may be one of the collateral effects of larger grain size, it is certainly one of the characteristics that tool hardeners have termed as "body," and which we now call "timbre." These minute cracks are undoubtedly the forerunners of the larger gross cracks that we encountered in this steel, as reported in the paper.

We have made no quantitative determinations in regard to the amount of retained austenite in any of these steels. However Bain shows that between 20 and 25 per cent of austenite can be retained by similar methods of heat treating. We have established the fact that austenite is retained by size change determinations.

The ¼-inch gage length of the test specimens was hardened through the entire cross section. A specimen with these characteristics was purposely selected since fundamental information can only be obtained on a structure representing the case of a hardened tool. The problem of compound sections is greatly influenced by amount and hardness of the core, design of the tool, etc., and these are some of the practical considerations which must be kept in mind in applying the impact results to practical cases.

We are indeed indebted to Dr. de Forest for his remarks which aid in answering questions raised by several of the discussors.

Mr. Hall's question in regard to the cross arm "h" in Fig. 2 being omitted in the photograph Fig. 3 can be easily answered. The cross arm is

present in the photograph of Fig. 3, but is in a very flat perspective, and consequently cannot be easily seen. Mr. Hall is entirely right in assuming that the friction wheel which drives the flywheel "c" is disengaged after bringing the machine up to speed before breaking the specimen.

In answer to Mr. Hall's question in regard to atmosphere, it is quite likely that all atmospheres in the furnace represent slower heating than those of the lead pot. The oxidizing atmosphere may be faster due to the fact that some of the scale formed does not adhere as tightly to the specimen as in a reducing atmosphere.

The fact that with greater drawing time the maximum impact is secured for lower drawing temperatures without particular increase in actual value is quite likely due to the fact that we are dealing simply with reaction speeds in a relatively small section. It is further quite possible that not only structural changes take place more rapidly in the specimen used, but stresses are more completely drawn out in a given time than they would be in a large tool in the same time. It should be pointed out again that the data obtained from the torsion impact machine is fundamental information in regard to the behavior of the hardened case of a tool of carbon steel, and that all of these results should be applied with considerable care.

THE ACTION OF OXYGEN AND HYDROGEN SULPHIDE UPON IRON-CHROMIUM ALLOYS AT HIGH TEMPERATURES

R. L. Rickett and W. P. Wood

Abstract

The action of oxygen and hydrogen sulphide upon iron-chromium alloys at high temperatures was investigated with the determination of the mechanism of reaction as the principal object.

The alloys that were studied contained up to 28 per cent chromium. The temperature range covered in the investigation was from 760 to 1095 degrees Cent. (1400 to 2000 degrees Fahr.), and exposure times up to 150 hours were used. The gain in weight of the specimens was measured, and the chemical composition, microstructure, and crystal structure of typical specimens of scale were investigated.

Hydrogen sulphide was found to cause much greater scaling than oxygen under similar conditions. Increasing amounts of chromium greatly increased the resistance to oxidation but only slightly increased the resistance to attack by hydrogen sulphide under the conditions of this work.

The effect of alloy composition and type of atmosphere is explained on the basis of the type of scale produced and the consequent variation in rates of diffusion through the scale. The compositions of the various types of scale are also explained on the basis of diffusion. The effects of temperature and of time were found to be consistent with a diffusion hypothesis.

ALLOYS suitable for use at high temperatures have become increasingly important during the last few years. The properties of these alloys that are of interest in connection with such use are their physical properties at high temperatures and their resistance to continued attack by the atmospheres in which they are used. A

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very large number of papers dealing with the physical properties of metals and alloys at elevated temperatures has appeared and much work along this line is now being done. The subject of resistance to deterioration at high temperatures through the action of the atmospheres encountered in service has, on the other hand, received very little attention in the technical literature in spite of the importance of such action in many applications.

The resistance of metals and alloys to attack by gases at high temperatures may be investigated with the object of obtaining quantitative data as to the amount of attack under definite conditions or with the aim of determining the mechanism of reaction. A knowledge of the mechanism of attack is essential to an understanding of the behavior of the so-called heat resistant alloys that are in use and would be of great value in developing new alloys. The present paper gives the results of an investigation to determine the nature of the action of corrosive gases upon heat resistant alloys so far as is possible from a study of the action of oxygen and hydrogen sulphide upon iron-chromium alloys. Chromium in sufficient quantities is known to confer marked resistance to oxidation, and the iron-chromium alloys possess most of the heat resistant characteristics of the more complex alloys. Oxygen and hydrogen sulphide were selected for this investigation because they are two fairly typical and quite different corrosive agents.

Although the mechanism of attack was the principal object of this investigation, it was first necessary to obtain definite data as to the effect of various factors upon the amount of attack. This paper is, therefore, divided into two parts. In Part I are considered the effects of time, temperature, type of atmosphere, and alloy composition upon the amount of attack, and in Part II there is developed a possible mechanism of reaction from a consideration of the data given in Part I, and the results of an examination of the products of reaction.

Part I

Data on the Action of Oxygen and Hydrogen Sulphide Upon Iron-Chromium Alloys at High Temperatures

The technical literature and the work of the authors concerning the action of oxygen and hydrogen sulphide upon iron-chromium alloys at high temperatures will now be considered.

Discussion of Literature

Only a few of the articles that deal with the oxidation of iron-chromium alloys give the actual results of experimental work. One such article is that of Hatfield[1] who determined the amount of scaling in oxygen of alloys that contained 13 and 18 per cent chromium. This work covered the temperature range from 700 to 1000 degrees Cent. (1290 to 1830 degrees Fahr.). Hatfield found that at 700 degrees Cent. there was little difference in the amount of oxidation of the two alloys, but as the temperature increased the rate of oxidation of the lower chromium alloy increased much more rapidly than that of the higher chromium alloy. Mathews[2] has reported the results of oxidation tests of iron-chromium alloys that contained from 13 to 26 per cent chromium. From his data no direct comparisons of different alloys are possible, but the temperature at which a considerable amount of scale was produced increased as the chromium content of the alloys increased. Schmidt and Jungwirth[3] found that alloys containing 28 to 30 per cent chromium scaled less at 1000 degrees Cent. (1830 degrees Fahr.) than did those containing 20 to 24 per cent chromium, and very much less than the latter at 1100 degrees Cent. (2010 degrees Fahr.). MacQuigg[4] does not give any actual experimental results, but he states that the iron-chromium alloys show a marked increase in resistance to oxidation up to 9 per cent chromium, that from 9 to 20 per cent chromium, the resistance continues to increase but at a slower rate, while above 20 per cent chromium there is another sharp increase in the resistance to oxidation.

Most of the published work on the action of hydrogen sulphide upon iron-chromium alloys is concerned with temperatures of 500 degrees Cent. (930 degrees Fahr.) or below. Some results determined by Scholl and published by French[5] indicate that at 480 degrees Cent. (895 degrees Fahr.) the amount of attack in hydrogen sulphide decreases continuously as the chromium content increases up to about 18 per cent, and that beyond this chromium content there is little

[1]Hatfield, *Journal,* Iron and Steel Institute, Vol. 115, 1927, p. 483-522.

[2]Mathews, *Industrial and Engineering Chemistry,* Vol. 21, 1929, p. 1158-64.

[3]Schmidt and Jungwirth, *Archiv für d. Eisenhüttenwesen,* Vol. 5, 1932, p. 419-26.

[4]MacQuigg, *Transactions,* American Institute of Mining and Metallurgical Engineers, Vol. 69, 1923, p. 831, *Proceedings,* American Society for Testing Materials, Vol. 24 II, 1924, p. 373-82. A.S.T.M. High Temperature Symposium, 1931, p. 432-49.

[5]French, *Transactions,* American Electrochemical Society, Vol. 50, 1926, p. 47.

further change. White and Marek,[6] and also Sayles,[7] found that increasing amounts of chromium up to 20 per cent slightly decreased the amount of attack by hydrogen sulphide at 500 degrees Cent. (930 degrees Fahr.). White and Marek also found that the rate of reaction increased as the time increased. Wellmann[8] found that at 550 degrees Cent. (1020 degrees Fahr.) an alloy containing 23 per cent chromium scaled considerably less in hydrogen sulphide than did one that contained 14 per cent chromium. A 25 per cent chromium alloy was found by Gruber[9] to be attacked nearly as much as was pure iron when exposed in hydrogen sulphide at temperatures of 800 and 1000 degrees Cent. (1470 and 1830 degrees Fahr.). The action of sulphur-containing gases at relatively low temperatures has also been investigated in connection with studies of corrosion of oil refinery equipment.[10, 11, 12] In this work some increase in resistance to attack with increasing chromium additions has been found.

Scope of Investigation

It may be well to point out here that this investigation was not carried out with the idea that the experimental values obtained could be used directly to predict the amount of attack in service under a given set of conditions. In practical applications of the alloys a large number of factors are involved, and reliable data regarding the behavior of iron-chromium alloys under such conditions can only be obtained in the laboratory when all these factors are known and taken into account. The aim of the present work was rather to determine the specific effects of such factors as might be used to determine the nature of the reactions that take place at high temperatures between iron-chromium alloys and the gases under consideration.

With this in mind, the principal factors selected for study were time, temperature, and alloy composition. Periods of time up to 150 hours were used in the oxidation tests, and up to 50 hours in the work on hydrogen sulphide. The temperature range covered was from 760 to 1095 degrees Cent. (1400 to 2000 degrees Fahr.). Alloys that contained up to 28 per cent chromium were exposed for differ-

[6] White and Marek, *Industrial and Engineering Chemistry*, Vol. 24, 1932, p. 859-61.

[7] Sayles, *Fuels and Furnaces*, Vol. 8, 1930, p. 835.

[8] Wellmann, *Zeit. für Elektrochemie*, Vol. 37, 1931, p. 142-56.

[9] Gruber, *Zeit. für Metallkunde*, Vol. 23, 1931, p. 151-7.

[10] Duff, *Proceedings*, American Petroleum Institute, Vol. 11, 1930, p. 155-7.

[11] Whitman and Roberts, Ibid, Vol. 11, 1930, p. 150-4.

[12] Kendall and Speller, *Metal Progress*, Vol 19, February, 1931, p. 40.

ent periods of time at a temperature of 980 degrees Cent. (1800 degrees Fahr.), and at different temperatures for a 25-hour period. The compositions of the alloys used are given in Table I.

Table I
Compositions of Alloys

Alloy	Composition — Per Cent						
	Chromium	Carbon	Manganese	Silicon	Phosphorus	Sulphur	Nickel
R	0	0.22	1.48	0.02	.....	0.033	....
AA	10.93	....	0.39	....	.....	.....	....
HL	12.33	0.12	0.57	....	.....	.....	....
HN	10.93	....	0.39	....	.....	.....	....
AC	16.91	....	0.49	....	.....	.....	....
CL	20.32	0.20	0.42	....	.....	.....	0.26
CN	19.50	....	0.37	....	.....	.....	....
AB	26.82	....	0.83	....	.....	.....	....
FL*	28.53	0.16	0.45	0.40	0.027	0.020	0.22

*Analysis by courtesy of The Midvale Company.

Procedure

The action of oxygen and hydrogen sulphide upon iron-chromium alloys was determined by exposing specimens of the alloys to the action of these gases under definite conditions and measuring the gain in weight. The furnaces that were used consisted of fused silica tubes wound with chromel wire and packed in silocel. The tubes were 1½ inches in internal diameter and 30 inches long, and were wound with the wire for about 15 inches along the central portion. The ends were closed with rubber stoppers through which were inserted a glass inlet tube and a porcelain thermocouple protection tube at one end, and a glass outlet tube at the other end. This outlet tube dipped into mercury to form a seal.

Oxygen from commercial tanks was used. This gas was dried by being passed through tubes filled with anhydrous calcium chloride, but not otherwise purified. The amount of oxygen supplied to each furnace was measured by means of a flow gage that indicated the pressure drop through a constricted tube, a U-tube containing glycerine being used to measure this drop in pressure. The flow gages were calibrated by determining the time necessary to displace a measured volume of water at different rates of flow of gas. A pressure regulator was found convenient in maintaining a steady flow of gas to the furnaces. This pressure regulator consisted of a glass tee in the gas line, one arm of which dipped into mercury for an adjustable distance. The flow of gas could be set at a value slightly greater than that required for the furnace and the excess then bubbled out through the mercury with the result that a slight drop in pressure

at the tank did not reduce the flow of gas to the furnace. The depth of immersion of the end of the outlet tube from each furnace was also adjustable, and was regulated so that a positive pressure of about ½-inch of water was maintained within the furnaces. The amount of oxygen supplied to each furnace was 30 cubic centimeters per minute (at room temperature).

In the work with hydrogen sulphide the gas was diluted with nitrogen so that the mixture contained about 20 per cent by volume of hydrogen sulphide. This was done in order to obtain a more rapid flow of gas through the furnace without using too large quantities of hydrogen sulphide. This gas is readily decomposed at high temperatures, and, unless the rate of flow is fairly rapid, a large proportion of the sulphur vapor that results from the decomposition diffuses back to the inlet end of the furnace where it condenses. The hydrogen sulphide that was used was obtained from tanks of the compressed gas. It was not purified in any way except for the removal of water vapor by anhydrous calcium chloride. Nitrogen of the best grade obtainable commercially was used, and contained less than 0.3 per cent of oxygen. This amount of oxygen was sufficient to form a considerable amount of oxide in the scale and had to be removed as completely as possible before the gas was used. The removal of oxygen was accomplished by passing the gas through alkaline pyrogallate solution and then over phosphorus. The gas was then thoroughly dried with calcium chloride, ascarite, and phosphorus pentoxide in series. Any remaining oxygen was removed by passing the gas over fine iron turnings at 700 degrees Cent. and metallic calcium at 400 degrees Fahr. The rates of flow of the two gases were adjusted and measured separately by means of pressure regulators and flow gages of the same type as were used for oxygen. The gases were mixed just before they reached the furnaces and the rate of flow of the mixed gas was 60 cubic centimeters per minute (at room temperature). Analyses were made at intervals of the gas entering and leaving the furnace. The gas was collected and analyzed over mercury, sodium hydroxide solution being used as an absorbent for hydrogen sulphide. Mercury is slowly attacked by hydrogen sulphide but if the mercury is dry the rate of attack is not rapid enough to materially affect the results.

Temperature measurements were made with chromel-alumel thermocouples and a portable potentiometer. Porcelain tubes were used to protect the thermocouples from the furnace atmosphere. The

thermocouples were calibrated periodically by comparison with a noble metal couple that was used as a laboratory standard and was, in turn, checked at intervals with a similar couple calibrated by the Bureau of Standards. The temperature variation during a run was kept within ± 7 degrees Cent.

The specimens were cut from round bars either ½-inch or ⅜-inch in diameter and were about 1½ inches long. They were first filed to removed scale and surface irregularities and then finished with various grades of emery cloth and emery paper, the final polish being with No. 00 emery paper. They were then stamped on one end, washed in alcohol and ether successively, and weighed to the nearest 0.5 milligram.

The specimens were placed in the center of the heated portion of the furnaces so that they nearly touched the ends of the thermocouple protection tubes. They were mounted on supports made by wiring together two small unglazed porcelain tubes with platinum wire. For the tests in oxygen the furnaces were brought to the desired temperature before the specimens were inserted. At the end of a run the specimens were removed without cooling the furnace and were placed in metal boxes to cool so that any scale that might fall off during cooling could be collected. In the case of the tests in hydrogen sulphide it was necessary to avoid any possibility of oxidation of the specimens. They were therefore placed in the cool furnace which was then flushed with purified nitrogen and brought up to the desired temperature after which the hydrogen sulphide was turned on. This procedure was reversed at the end of a run.

The amount of attack during a run was determined by measuring the gain in weight. This was necessary because no satisfactory method could be found for removing the scale that was formed. The specimens heated in oxygen could be easily removed from the supports before weighing. When hydrogen sulphide was used it was difficult to remove the specimens from the supports and therefore the supports and specimens were weighed together before and after the runs. The areas of the specimens were measured before the tests, and the amount of scaling was expressed as the gain in weight per unit area of the original specimens.

Results

Effect of Time—The effect of time upon the reaction of oxygen and of hydrogen sulphide upon iron-chromium alloys at 980 degrees

Cent. (1800 degrees Fahr.) is shown in Figs. 1 and 2, respectively.

The curves given in Fig. 1 show that the rate of oxidation of the alloys containing 0, 12, 17, and 28 per cent chromium decreased continuously as the time increased. The results obtained with the

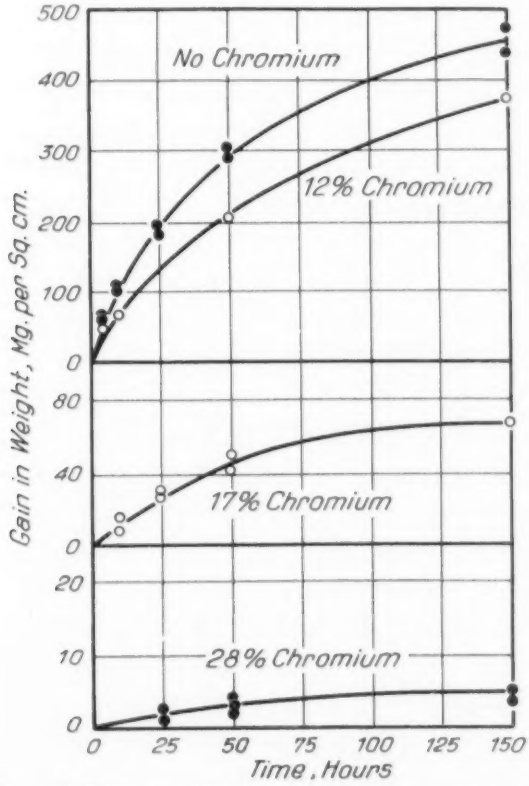


Fig. 1—Effect of Time on Amount of Oxidation at 980 Degrees Cent.

20 per cent chromium alloy varied so much that the form of the time-oxidation curve for this alloy could not be determined.

In order to determine the forms of the curves shown in Fig. 1, the same results were plotted using logarithmic scales for the time and the gain in weight. The points as thus plotted showed slight but definite deviations from straight lines over certain portions of the range. However, it was possible to represent the course of oxidation of each alloy on this type of graph by a straight line from which none of the points deviated by more than 10 per cent. From these straight lines the following equations were derived to represent the course of oxidation of the various alloys:

0 chromium alloy, $W^2 = 1440t$
12 per cent chromium alloy, $W^{1.6} = 108t$
17 per cent chromium alloy, $W^{1.5} = 6t$
27 per cent chromium alloy, $W^{1.35} = 0.05t$,

where W is the gain in weight in milligrams per square centimeter after a period of exposure of t hours. These equations show that as the chromium content of the alloys increases the exponent becomes more nearly unity, or in other words the amount of oxidation is more

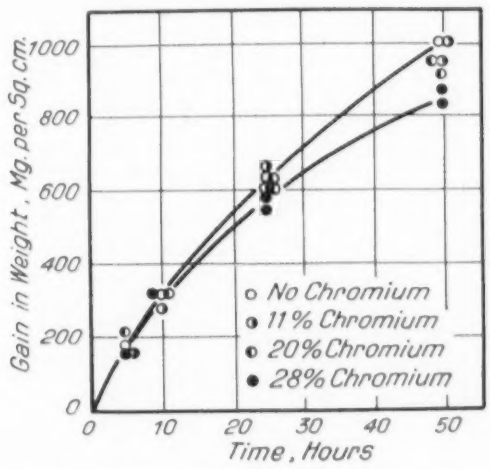


Fig. 2—Effect of Time on Amount of Reaction with Hydrogen Sulphide at 980 Degrees Cent.

nearly proportional to the time. The value of the proportionality factor in the equations is seen to decrease very markedly as the chromium content increases.

The effect of time upon the amount of sulphur that reacted with the alloys when exposed in hydrogen sulphide at 980 degrees Cent. (1800 degrees Fahr.) is shown in Fig. 2. The results are similar to those obtained with oxygen in that the amount of sulphur in combination with the metal increased as the time of exposure increased but at a decreasing rate. When these results were plotted using logarithmic coordinates the points were found to follow straight lines within the limits of the experimental error. The equations for these lines were found in the same way as were those for oxygen and the results are as follows:

0 chromium alloy, $W^{1.2} = 100t$
11 per cent chromium alloy, $W^{1.2} = 93t$
20 per cent chromium alloy, $W^{1.3} = 199t$
28 per cent chromium alloy, $W^{1.3} = 170t$

In these equations W is the gain in weight in milligrams per square centimeter and t is the time in hours, as before. These equations show that the amount of attack in hydrogen sulphide was more

nearly proportional to the time of exposure than in the case of oxygen. The amount of attack after a given time of exposure was also much greater in an atmosphere of hydrogen sulphide than in oxygen as may be seen by comparing Figs. 1 and 2.

Effect of Temperature—The effect of temperature upon the amount of oxidation in 25 hours is shown in Fig. 3. The rate of oxidation of the alloys that contained 12 and 20 per cent of chro-

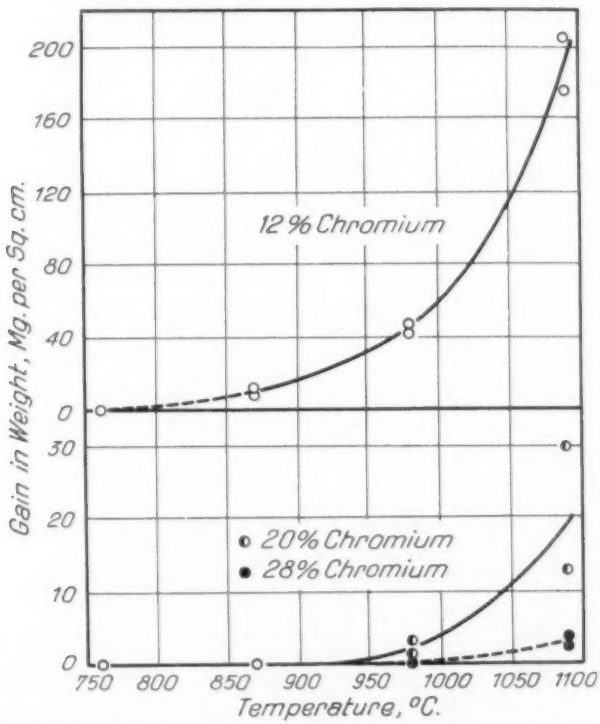


Fig. 3—Effect of Temperature on Amount of Oxidation in 25 Hours.

mium increased slowly at first and then much more rapidly as the temperature increased. The 28 per cent chromium alloy did not show any such great increase in rate of oxidation as the temperature was increased up to 1100 degrees Cent. It was found that the solid portions of the curves in Fig. 3 could be represented by equations of the form:

$$\log W = kT, \text{ or } W = a^{bT}$$

In these equations W is the gain in weight per unit area, T is the temperature in degrees Centigrade, and k, a, and b are constants. The portions of the curves shown as dotted lines did not follow these equations or at least did not have the same constants as the rest of the curve for the same alloy.

Fig. 4 shows the effect of temperature upon the amount of reaction in 25 hours in hydrogen sulphide. Only two alloys were selected for this work since the difference between the different alloys was found to be so slight. It was found that the following equations fitted the curves shown in Fig. 4 very well:

11 per cent chromium alloy,
$$W = -1.555T + 0.002225T^2$$

28 per cent chromium alloy,
$$W = -1.440T + 0.00198T^2$$

In these equations W is the gain in weight in milligrams per square centimeter in 25 hours and T is the temperature in degrees Centi-

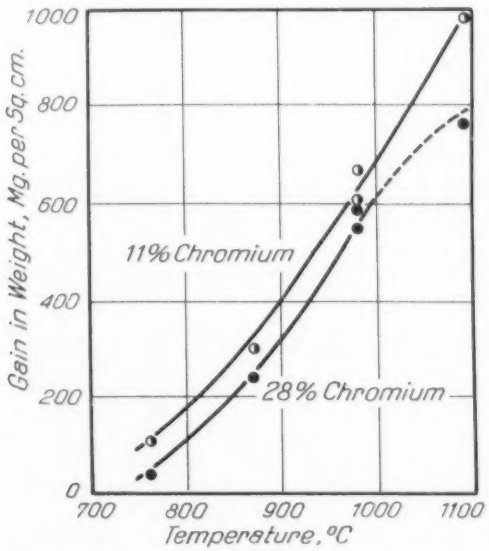


Fig. 4—Effect of Temperature on Amount of Reaction with Hydrogen Sulphide in 25 Hours.

grade. It is seen from a comparison of Figs. 3 and 4 that over the temperature range investigated the increase in rate of attack was more nearly proportional to the increase in temperature in the case of hydrogen sulphide than in the case of oxygen.

Effect of Composition—The effect of increasing amounts of chromium on the amount of oxidation is shown in Figs. 5 and 6. Fig. 5 shows that at a temperature of 980 degrees Cent. the most rapid increase in resistance to oxidation occurred between about 10 and 20 per cent chromium. The resistance increased slowly as the chromium content increased above 20 per cent, but there was probably

not much further change above 25 per cent chromium at this temperature. As the temperature increased the chromium content at which the curves began to flatten out also increased as is shown in Fig. 6. A similar variation in resistance to oxidation has been shown by Hauttmann[13] in the case of iron-aluminum alloys.

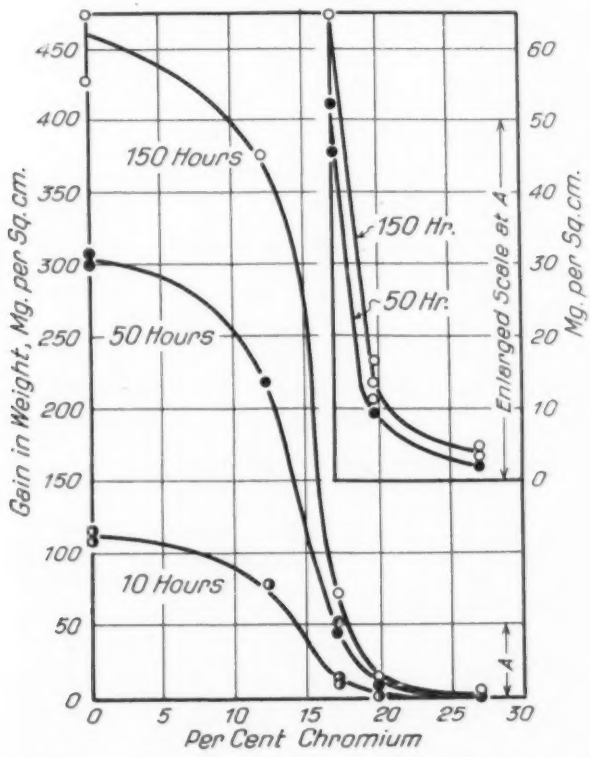


Fig. 5—Effect of Chromium Content on Amount of Oxidation at 980 Degrees Cent.

The effect of alloy composition upon the amount of attack when the various alloys were heated in hydrogen sulphide at 980 degrees Cent. (1800 degrees Fahr.) is shown in Fig. 7. On exposing the alloys for comparatively short periods of time there was no consistent variation in amount of attack with variations in chromium content. However, when the period of exposure was longer and the thickness of the scale correspondingly greater there was found a slight decrease in the amount of attack as the chromium content of the alloy increased. This decrease was very much less marked than in the tests made in oxygen.

Effect of Gas Velocity—In order to determine the effect of gas velocity on the amount of oxidation the 11 and 28 per cent chromium

[13]Hauttmann, *Stahl und Eisen*, Vol. 51, 1931, p. 65-7.

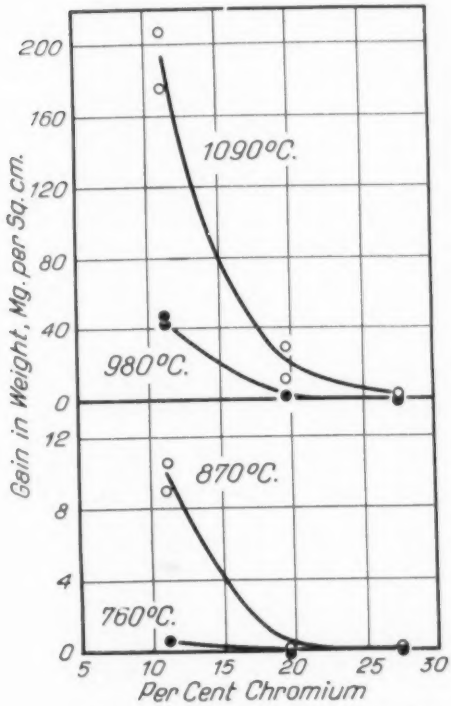


Fig. 6—Effect of Chromium Content on Amount of Oxidation in 25 Hours.

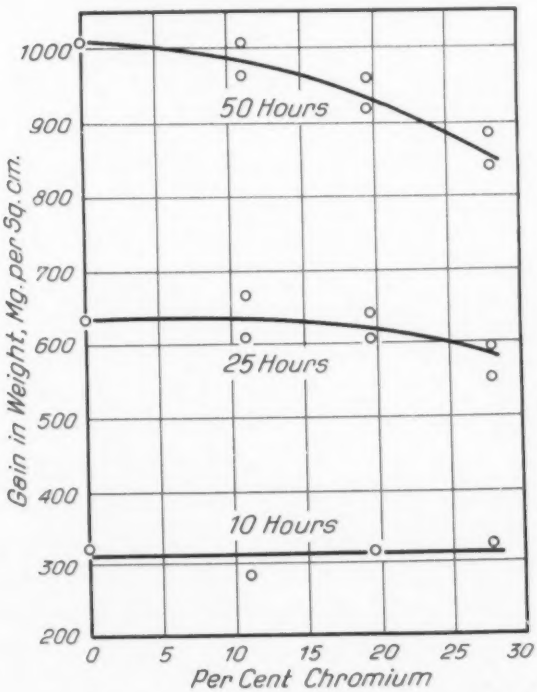


Fig. 7—Effect of Chromium Content on Amount of Reaction with Hydrogen Sulphide at 980 Degrees Cent.

alloys were heated for 25 hours at 980 degrees Cent. in a stream of oxygen supplied at a rate of 90 cubic centimeters per minute (at room temperature) instead of the 30 cubic centimeters per minute used in the rest of the work. No significant variations in amount of oxidation were found. Similar tests in hydrogen sulphide using ½ and 1½ times the usual flow of gas likewise showed no evidence of any effect on the rate of attack.

Part II

The Mechanism of Reaction of Oxygen and Hydrogen Sulphide with Iron-Chromium Alloys

In the remainder of this paper the literature dealing with the mechanism of reaction of gases with metals and alloys in the solid state will be considered, and a mechanism of reaction of oxygen and hydrogen sulphide with iron-chromium alloys will be developed from a consideration of the results given in Part I, and the data secured by investigating the products of reaction.

Review of Literature

An important contribution to the subject of the mechanism of oxidation of metals at high temperatures was made by Pilling and Bedworth.[14] These authors classify metals as noble and base according to whether their oxides have relatively high or low dissociation pressures. They postulate that the oxidation of base metals takes place at the metal oxide interface and that two types of oxides may be formed. If the oxide layer is cellular then it offers little resistance to further oxidation and the rate of oxidation at a given temperature is constant. When a compact oxide is formed, further oxidation must take place by the diffusion of oxygen through the layer of oxide already formed, and at a given temperature the rate of oxidation is inversely proportional to the thickness of this oxide layer. The theory of Pilling and Bedworth has been criticized because it postulates that all oxidation takes place at the oxide-metal interface so that the scale must be plastic if oxidation is to continue without cracking the scale already formed. Pfeil[15] has made a contribution to the theory of oxidation that eliminates this difficulty. He observed that the scale formed by the oxidation of iron consisted,

[14]Pilling and Bedworth, *Chemical and Metallurgical Engineering*, Vol. 27, 1922, p. 72-4.

[15]Pfeil, *Journal*, Iron and Steel Institute, Vol. 119, 1929, p. 501-547.

in general, of three layers, and that the boundary between the inner and middle layers corresponded in position and appearance to the original surface of the specimen. He also found that particles of foreign materials placed on the surface of the specimen were enveloped by the scale without change of position. From these observations Pfeil concluded that there must be a diffusion of iron outward as well as a diffusion of oxygen inward. In some work by Murphy[16] and his associates it has been shown that, in addition to the diffusion of the oxidizing gas inward and the metal outward, it may be necessary, in some instances, to take into consideration the rate of diffusion of gaseous products of reaction outward through the scale.

Several investigations of the oxidation of alloys have shown that different layers of the scale produced may contain vastly different proportions of the alloying elements. Thus, Dunn[17] found in a study of the oxidation of copper-zinc alloys that alloys containing from 60 to 75 per cent copper formed a scale that consisted largely of zinc oxide, that the scale on alloys of from 78 to 86 per cent copper consisted of an outer layer of cupric oxide, a middle layer of zinc oxide, and an inner layer of cuprous oxide, while alloys higher in copper formed a scale that consisted largely of copper oxides. Dunn explains the absence of appreciable amounts of copper oxide in the scale formed on the alloys lower in copper on the hypothesis that the rate of diffusion of zinc in these alloys is sufficient to reduce copper oxide as fast as it is formed, or in other words that there is, in effect, a preferential oxidation of the zinc. He does not explain the results obtained in the case of the alloys that contain from 78 to 86 per cent copper. Hauttmann[18] has also proposed a theory of selective oxidation to account for the fact that the scale formed on iron-aluminum alloys that contained 9 per cent or more of aluminum consisted principally of aluminum oxide while on alloys that contained less than 4 per cent aluminum the scale appeared to mostly consist of iron oxides.

Pfeil[15] has published results that do not accord with the hypothesis of preferential oxidation. He has shown that the oxidation of a large number of alloys of iron with other elements results in the

[16]Murphy, Wood, and Jominy, TRANSACTIONS, American Society for Steel Treating, Vol. 19, 1932, p. 193-246.

[17]Dunn, *Journal*, Institute of Metals, Vol. 46, 1931, p. 25-52.

[18]Loc. cit.

[15]Loc. cit.

formation of three layers of scale, of which the outer layer contains a higher proportion of iron, and the inner layer a lower proportion of iron than the original alloy. This was found to be true both in the case of alloys of iron with elements that have a greater affinity for oxygen and those that have a lower affinity for oxygen than has iron. Dunn[17] found that the scale formed on a copper-silicon alloy containing up to 5 per cent silicon was practically free from silica, which is not in accord with his theory of preferential oxidation since silicon forms a much more stable oxide than does copper. It thus appears that no adequate explanation has been given to account for the varying proportions of the alloying elements found in the scale formed by the oxidation of alloys.

A Mechanism of Scaling

It remains now to develop a mechanism of scaling that will account for the effects of time, temperature, alloy composition, and nature of the atmosphere on the action of oxygen and hydrogen sulphide on iron-chromium alloys.

Reaction of Gases at High Temperatures with Alloys in the Solid State—It may be well at this point to consider what happens when an alloy is exposed to a gas with which it reacts. If the component metals of the alloy are all capable of reacting with the gas under the conditions of the test, then the first step is a chemical reaction between the gas and the surface layer of the alloy with the formation of a mixture or solid solution of those reaction products that are in equilibrium with the partial pressure of the reacting gas in the furnace atmosphere, and in which the component metals are in the same ratio as in the original alloy. If this layer of reaction products is physically continuous, then further reaction must involve diffusion into or through this layer and may also involve chemical reactions within the layer itself. There is the possibility that diffusion may take place in two directions through the layer of reaction products, inward and outward. It is obvious that there must be diffusion inward if scaling is to proceed, otherwise the metal-oxide interface would not be maintained and further scaling could only proceed by the evaporation of metal from the surface of the alloy and the transfer of this metal outward through the scale. It is highly improbable that there is any appreciable evaporation of either

[17] Loc. cit.

iron or chromium at the temperatures with which we are concerned here. The probability that metal or a product of reaction diffuses outward was first demonstrated by Pfeil who showed that in the case of the oxidation of iron the original surface of the metal was retained in position and form, even after scaling had proceeded to a considerable depth into the specimen. The present authors observed this same phenomenon in their work on the action of hydrogen sulphide on the iron-chromium alloys. Fig. 10 shows the clear outlines of the original surfaces of two specimens from which portions of the outer layers of scale had been removed.

Rate of Scaling—The problem of scaling is essentially one of reaction in a heterogeneous system. Two factors are involved in determining the velocity of such reactions; one is the actual velocity of chemical reaction at the interface between the reacting phases, and the second is the rate at which the products of reaction are removed from the interface, or in some cases the rate at which one or more of the reactants reaches the interface. This second factor obviously involves diffusion processes, and if the rate of diffusion is less than the rate of chemical reaction at the interface then the diffusion rates will determine the actual velocity of scaling.

It is of interest to determine whether the rate of chemical reaction or the rate of diffusion is the controlling factor in the reactions that were investigated in the present work. Taylor[18] cites figures compiled by Öholm which show that for diffusion processes the temperature coefficient per 10-degree rise is from 1.2 to 1.5, while if the rate of reaction is the controlling factor the temperature coefficients are greater and frequently range from 2 to 4 per 10-degree rise in temperature. In Table II are given values of the temperature coefficient per 10-degree rise for scaling in both oxygen and hydrogen sulphide as computed from the results of the present work. These coefficients are of the order of magnitude of those that were reported

Table II
Temperature Coefficient per 10 Degrees Cent. Rise in Temperature
25-Hour Tests at Temperatures Given

	Temperature Coefficient per 10 Degrees Cent.			
Alloy	Oxygen 900 Degrees Cent.	Oxygen 1050 Degrees Cent.	Hydrogen Sulphide 900 Degrees Cent.	Hydrogen Sulphide 1050 Degrees Cent.
12% chromium	1.25	1.15	1.14	1.10
20% chromium	1.0+	1.44	....	....
28% chromium	1.0+	1.72	1.14	1.09

[18]Taylor, Treatise on Physical Chemistry, Vol. II, 1931, p. 1025.

by Öholm for diffusion and are much less than those for chemical reactions. Therefore, it may be concluded that the rate of diffusion determined the rate of scaling in this work.

Proposed Mechanism of Scaling—On the basis of the foregoing considerations it is possible to offer the following hypothesis to explain the results of the present work:

1. The alloy first reacts with oxygen or hydrogen sulphide with the formation of a surface layer of those oxides or sulphides of iron and chromium that are in equilibrium with the partial pressure of oxygen or hydrogen sulphide in the furnace atmosphere, and in which the two metals are in the same ratio as in the original alloy.

2. After the formation of this initial layer of scale the rate of scaling is determined by the rate of diffusion of certain substances through the scale.

3. There is a diffusion of the reacting gas or of higher products of reaction inward and of the component metals of the alloy or of lower products of reaction outward through the scale. These diffusion processes may be accompanied by chemical reactions within the scale as well as the chemical reaction that takes place at the scale-metal interface.

Since diffusion is such an important factor it is worth while to consider the diffusion equation:

$$\frac{dW}{dt} = -\frac{Ddc}{dx}$$

In this equation $\frac{dW}{dt}$ is the rate of diffusion, D is the diffusion constant per unit of cross-sectional area, and $\frac{dc}{dx}$ is the concentration gradient. The diffusion constant depends upon the nature of the substance which is diffusing and the chemical composition and physical structure of the medium through which diffusion takes place. The concentration gradient depends upon the distance through which diffusion takes place and is limited by the maximum solubility of the substance that diffuses. From this equation it is evident that, where the rate of diffusion is the controlling factor, a high rate of scaling requires a high diffusion coefficient, high solubility of the reactant in the scale, or the occurrence of reactions within the scale that will increase the effective concentration gradients of the reactants. The

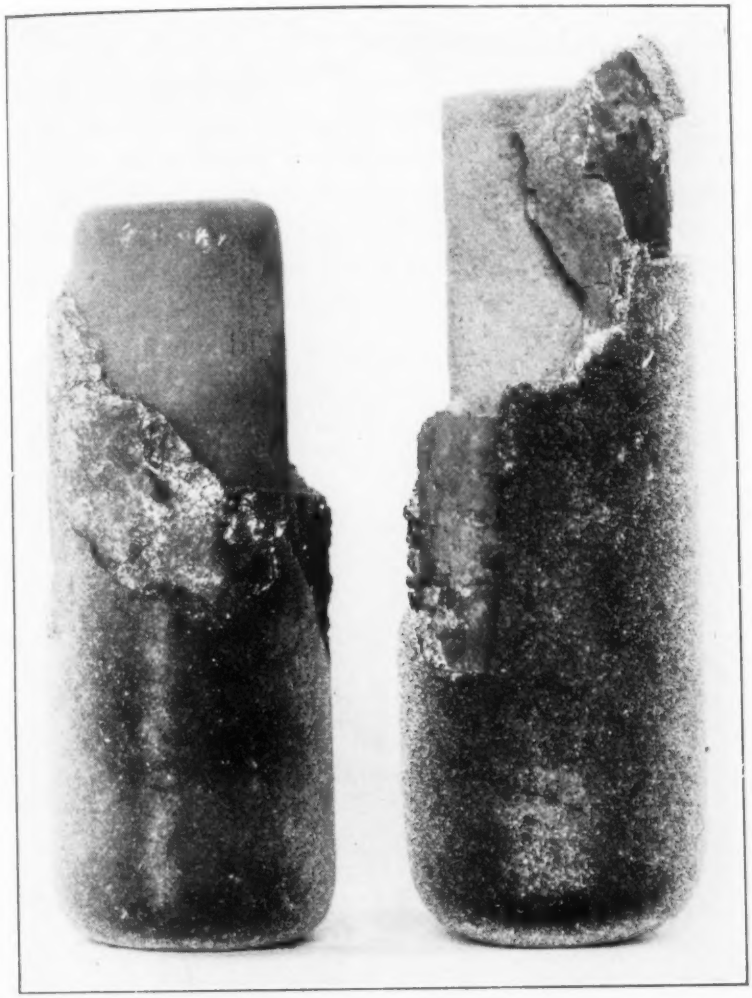


Fig. 8—Oxide Scale on Alloy Containing 12 Per Cent Chromium. Specimen at Left Heated 50 Hours and One at Right Heated 150 Hours at 980 Degrees Cent. (1800 Degrees Fahr.). Magnification 2.

authors wish to particularly emphasize the following three of the possible conditions.

1. Only one phase can be formed as the result of the reaction with each of the components of the alloy and the solubilities of the reactants in this phase are low. In this case the rate of scaling would be expected to be comparatively slow.

2. Only one phase can be formed as the result of the reaction with each of the components of the alloy but the solubilities of the reactants in this phase are high. The rate of scaling would be much greater than in the first case.

3. Two or more phases may be formed as the result of the

reaction and these phases may interact. In this case the rate of scaling may be comparatively rapid.

A determination of the chemical composition, crystal structure, and microstructure of the scale formed in oxygen and in hydrogen sulphide gave interesting information as to possible reasons for the behavior of the various alloys in the two gases. The results of this investigation of the scale will now be considered and will be followed by a discussion of various factors that affect scaling in view of these results and the proposed mechanism of scaling.

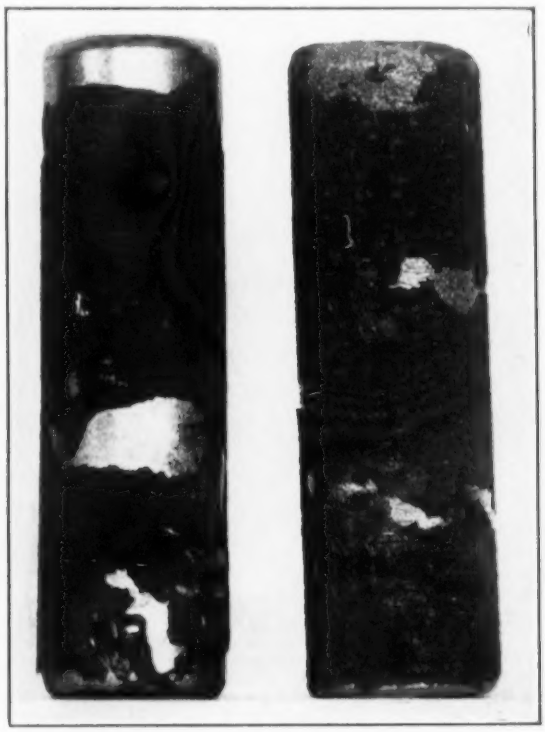


Fig. 9—Oxide Scale on Alloy Containing 28 Per Cent Chromium. Specimen at Left Exposed for 50 Hours and One at Right for 150 Hours at 980 Degrees Cent. (1800 Degrees Fahr.). Magnification 2.

Characteristics of Oxide and Sulphide Scale

General Characteristics of Scale—The appearance of the scale formed in oxygen on two of the iron-chromium alloys is shown in Figs. 8 and 9. Three distinct layers of scale were formed on the lower-chromium alloy. The outer layer was blue-gray in color while the other two layers were dark gray. The middle layer was the thinnest and the inner layer the thickest of the three. As the chro-

mium content of the alloys increased the number of distinct layers of scale decreased. On the alloy containing 28 per cent chromium there was formed an extremely thin single layer of scale that fell off readily after the specimens were cooled.

Fig. 10 shows the appearance of specimens heated in hydrogen sulphide. The alloy composition did not have much effect on the type of scale produced in this gas. The fact that the original outlines of the specimens were preserved during scaling in hydrogen sulphide has already been mentioned. Two layers of scale occurred outside

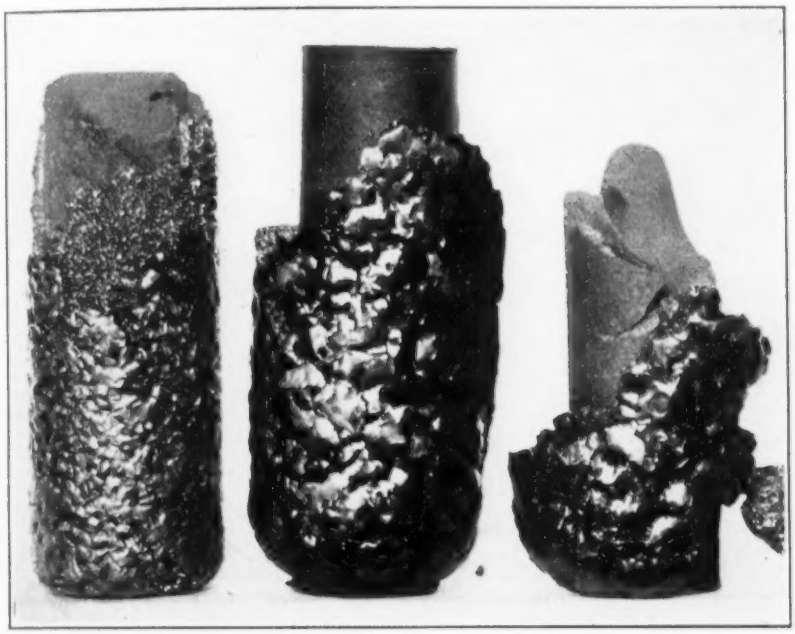


Fig. 10—Sulphide Scale on Alloy Containing 11 Per Cent Chromium. Specimens Exposed for 10, 25, and 50 Hours, Respectively, from Left to Right. Magnification 1.7.

this original surface and consisted of very coarse crystals of a brassy-yellow color. Three layers of scale could be distinguished inside the original surface but they could not be readily separated. These layers were gray in color and had a dull luster.

Chemical Composition of Scale—The composition of the scale formed on various alloys in oxygen is given in Table III, and the composition of that formed in hydrogen sulphide is given in Table IV.

The principal features shown by the oxide scale are the rapid increase in the proportion of chromium in the scale as the chromium content of the alloys increases and the higher proportion of chromium in the inner layer of scale as compared to the outer layer in cases

Table III
Chemical Composition of Oxide Scale

Per Cent Chromium in Alloy	Temp. Degrees Cent.	Time Hours	Layer of Scale	Per Cent Iron	Per Cent Chromium	Per Cent Manganese	Ratio: Cr / Cr+Fe+Mn × 100
12.33	980	50	Outer	70.0	None	*	0
12.33	980	150	Inner	57.02	18.58	*	24.55
20.32	980	50	Single	57.60	11.20	*	16.25
20.32	1090	50	Outer	64.60	4.45	*	6.44
20.32	1090	50	Inner	48.10	14.66	*	23.35
28.53	980	50	Single	6.20	55.78	5.32	81.40

*Manganese a few tenths of 1 per cent or less.

Table IV
Chemical Composition of Sulphide Scale

Per Cent Chromium in Alloy	Degrees Cent.	Time Hours	Layer of Scale	Per Cent Iron	Per Cent Chromium	Per Cent Sulphur	Ratio: Cr / Cr+Fe
10.93	980	50	Outer	60.50	0.49	37.35	0.8
			Second	48.55	11.05	38.83	18.5
			Remainder	43.75	15.70	36.20	26.4
28	980	50	Outer	59.95	0.98	37.30	1.6
			Second	39.05	19.37	39.75	33.2
			Remainder	26.80	32.55	38.53	54.5

FeS = 36.5% S.
CrS = 38.2% S.

where more than one layer was formed. This latter phenomenon was also observed by Pfeil[15] in the case of a number of alloys of iron, as has been mentioned. It is significant that the alloy that contained 28 per cent of chromium was by far the most resistant to oxidation of

Table V
Constituents in Oxide Scale

Alloy Per Cent Chromium	Temp. Degrees Cent	Time Hours	Layer	Constituents
12	980	150	Outer	Fe_2O_3 and Fe_3O_4
			Middle	$(Fe, Cr)_2O_3$ and $(Fe, Cr)_3O_4$
			Inner	$(Fe, Cr)_3O_4$
20	1090	50	Outer	$(Fe, Cr)_2O_3$
			Inner	$(Fe, Cr)_3O_4$
28	980	50	Single	$(Cr, Fe)_2O_3$ and $(Fe, Cr)_3O_4$

those investigated and formed a scale that consisted largely of chromium oxide.

The sulphide scale did not show as wide a variation in chromium content as the composition of the alloys varied from 11 to 28 per

[15]Pfeil, Loc. cit.

cent chromium. There was, however, a marked decrease in the proportion of chromium in the scale as the distance from the metal increased.

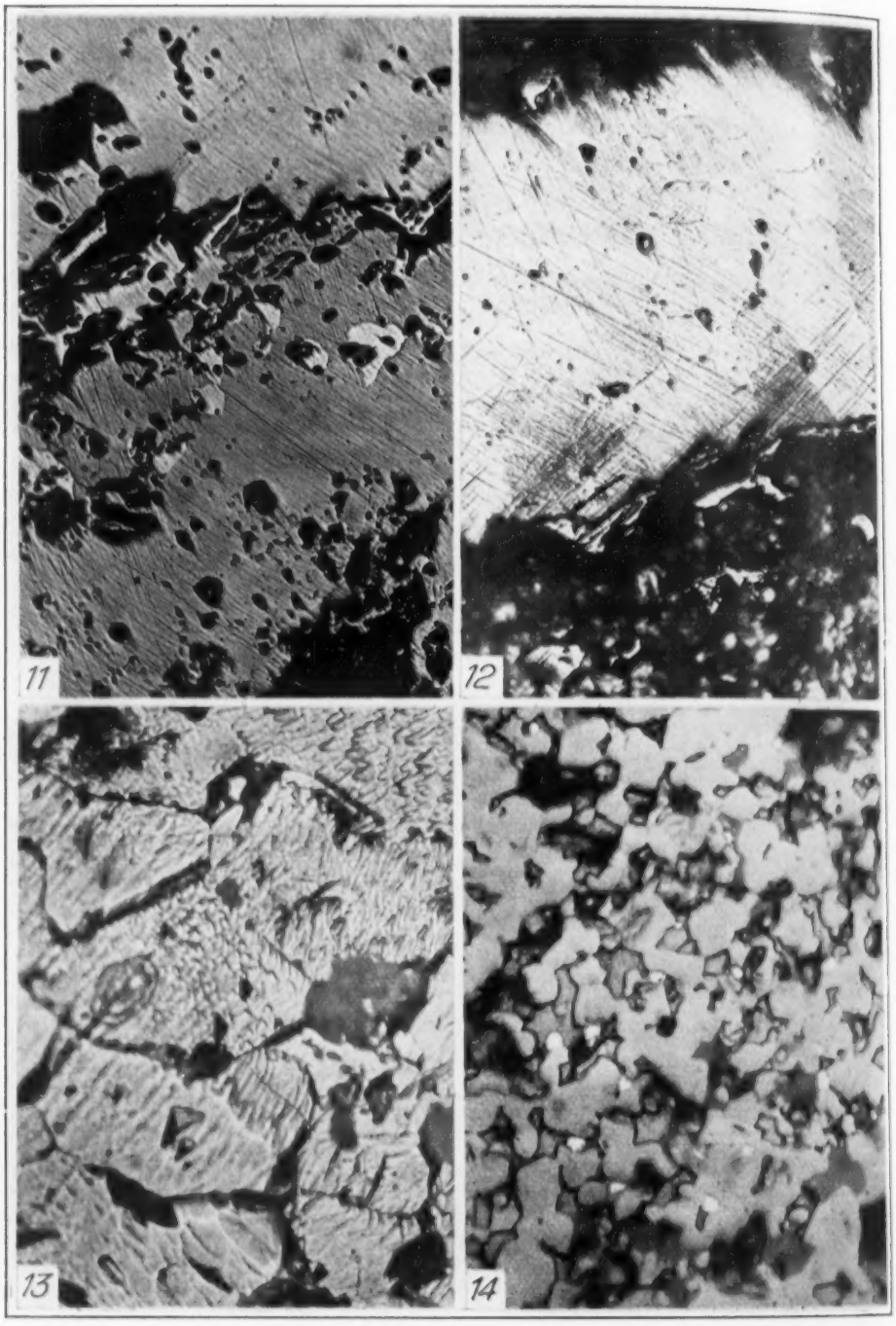
Crystal Structure of Scale—The constituents present in various layers of scale formed on the different alloys and the lattice dimensions of these constituents were determined by means of X-ray powder diagrams using sodium chloride as a reference substance. The space available here is too limited to present more than a small portion of the results of this work. Table V gives the constituents found in some of the oxide scales. It will be noticed that no evidence of the presence of ferrous oxide was found.

In the various layers of sulphide scale formed on alloys that contained 11 and 28 per cent chromium the principal constituent had the structure of FeS and from the results of the chemical analyses was evidently a FeS-CrS solid solution. A few lines due to a second, unidentified constituent were found in the powder diagrams of the three inner layers of scale.

Microstructure of Scale—It has already been mentioned that the number of distinct layers of the scale formed in oxygen decreased as the chromium content of the alloys increased. The appearance of the constituents of the scale also varied considerably with changes in chromium content of the alloys as shown in Figs. 11 to 16, inclusive. The method of mounting the specimens for polishing was essentially that described by Pfeil.[19] Severe pitting of the brittle scale occurred during polishing and could not be avoided even by using great care. In spite of the numerous pits the photomicrographs yield some definite information and so will be discussed briefly here.

The outer layer of scale formed on the 12 per cent chromium alloy in oxygen was found by chemical analysis to consist largely of iron oxides and from Fig. 11 is seen to consist of two constituents. X-ray analysis showed that Fe_2O_3 and Fe_3O_4 were present in this layer of scale. The outer portion then, is probably Fe_2O_3 and was found to be only slowly etched by concentrated hydrochloric acid, while the inner portion which is darker in color and was readily attacked by even dilute hydrochloric acid is evidently Fe_3O_4. The structure of the inner layer of scale on the same specimen is shown in Fig. 14, and is seen to contain at least four constituents. The identity of these constituents is uncertain but the white particles are

[19]Pfeil, *Journal*, Iron and Steel Institute, Vol. 123, 1931, p. 237-58.



12 Per Cent Chromium Alloy

Fig. 11—Outer Layer of Oxide Scale Formed at 980 Degrees Cent. and Cooled in Air. Unetched. × 100.

Fig. 12—Outer Layer of Scale from Same Specimen as Fig. 11. Heavily Etched in HCl. × 100.

Fig. 13—Dark Zone of Outer Layer of Oxide Scale More Lightly Etched than in Fig. 12. × 500.

Fig. 14—Third, or Inner, Layer of Oxide Scale Formed at 980 Degrees Cent. and Cooled in Air. Etched with Dilute HCl. × 1000.

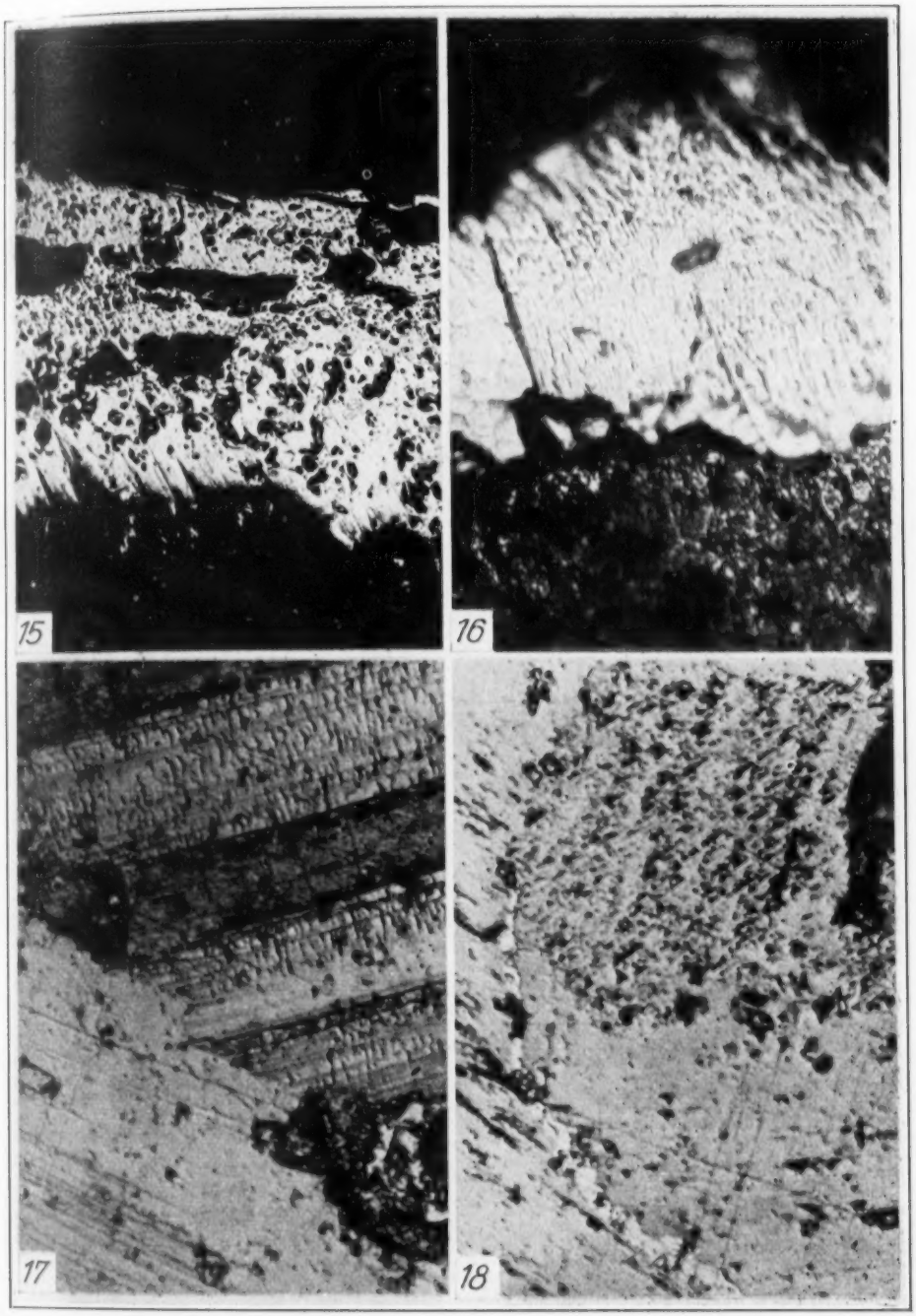


Fig. 15—Oxide Scale Formed on 17 Per Cent Chromium Alloy at 980 Degrees Cent. Unetched. When Etched, Outer Portion (at Bottom) was Slowly Attacked by Concentrated HCl and Remainder was Entirely Unattacked. × 100.

Fig. 16—Oxide Scale on 28 Per Cent Chromium Alloy Heated at 980 Degrees Cent. This Specimen was Polished at an Angle. Etched with Concentrated HCl. × 500.

Fig. 17—Outer Layer of Sulphide Scale on 28 Per Cent Chromium Alloy Heated at 980 Degrees Cent. Etched in Dilute HCl. × 1000.

Fig. 18—Second Layer of Scale on Same Specimen as Fig. 17. Etched in Dilute HCl. × 1000.

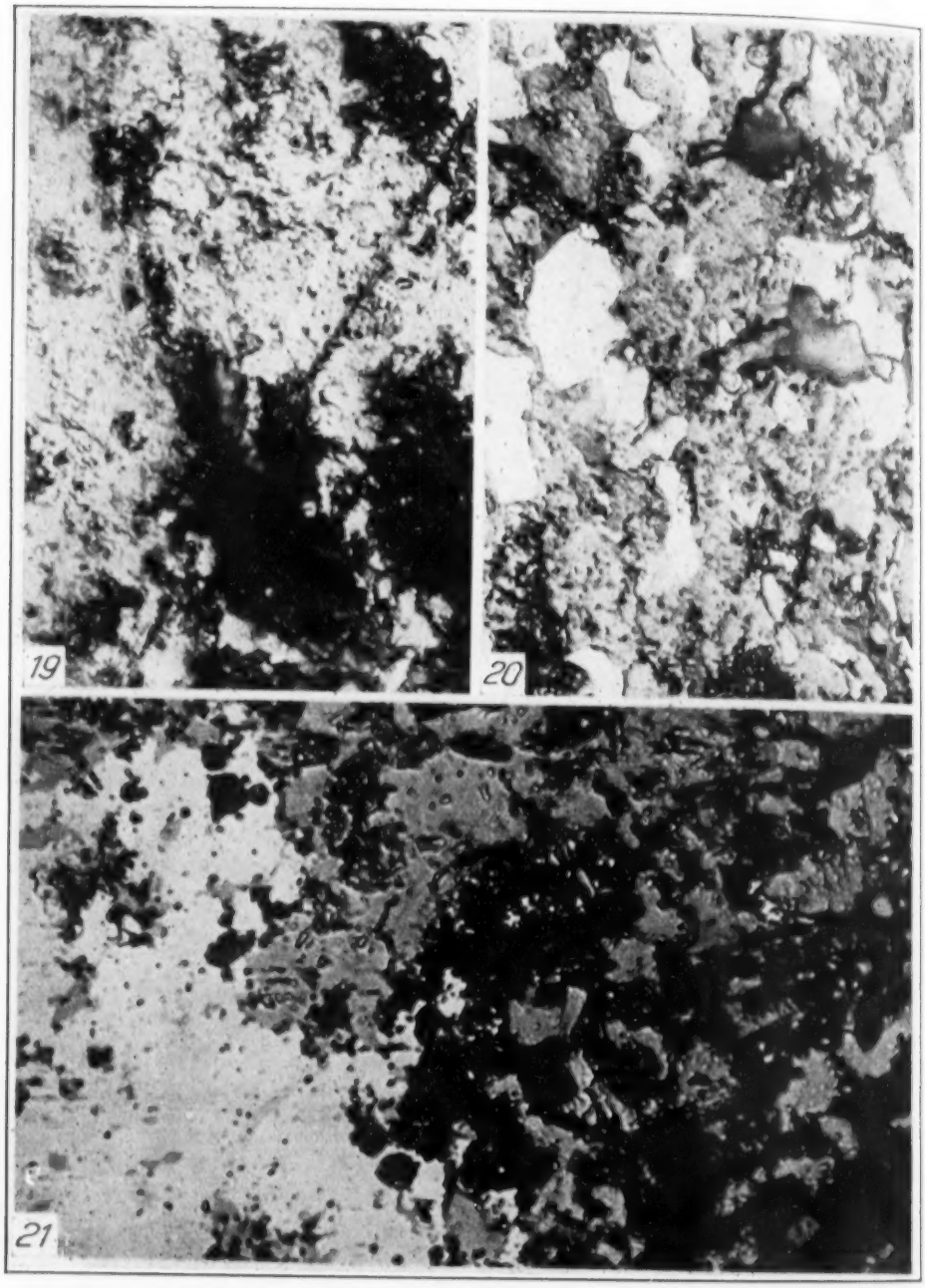


Fig. 19—Third Layer of Scale on Same Specimen as in Figs. 17 and 18. Etched in Dilute HCl. × 1000.

Fig. 20—Fifth, or Inner, Layer of Scale on Same Specimen as at Left. Etched in Dilute HCl. × 1000.

Fig. 21—Boundary Between Scale and Metal on Same Specimen as Fig. 17. Unetched. × 1000.

probably unoxidized metal while the unetched matrix is quite possibly chromite, $FeCr_2O_4$. This constituent was completely unattacked by concentrated hydrochloric acid, which is characteristic of chromite as described by Schneiderhölm and Ramdor.[20] The crystal structure of chromite is almost identical with that of Fe_3O_4 and was the only one found by X-ray analysis of this layer of scale.

On the alloy with 17 per cent chromium only one layer of scale was formed and the structure of this is shown in Fig. 15. The outer portion resembles that on the lower chromium alloy, was very slightly etched after long treatment with concentrated HCl, and is probably Fe_2O_3 with possibly some Cr_2O_3 in solid solution. The inner portion is lighter in color than the inner portion of the outer layer of scale on the 12 per cent chromium alloy and was unattacked by concentrated hydrochloric acid. It resembles the matrix of the inner layer of scale on the lower chromium alloy and is very probably chromite.

The structure of the single layer of scale formed on the 28 per cent chromium alloy in oxygen is shown in Fig. 16. Only one constituent is seen, although the X-ray results indicated two. The specimen shown was polished at an angle and may not represent a complete cross section of the scale. The results of chemical analysis showed a high proportion of chromium in this scale while most of the lines on the X-ray diagram corresponded to the structure of Cr_2O_3 which is probably the principal constituent of this scale.

The microstructure of the scale formed in hydrogen sulphide did not vary much with changes in chromium content, and therefore photomicrographs of the scale from only one alloy are shown. Figs. 17 to 21, inclusive, show the structure of typical portions of the scale found on a specimen of the 28 per cent chromium alloy. In the outer layer only one constituent was found as is shown in Fig. 17. Very pronounced twinning was observed in the outer layer of scale in this particular alloy, while in the scale formed on some of the other alloys the twinning occurred in other layers but in the same constituent. From the X-ray and chemical data this constituent appears to be a solid solution of FeS and CrS with probably some excess sulphur in solution. A second, lighter colored, constituent is seen in the second and remaining layers of scale and is most pronounced in the inner layer. This constituent has not been identified but a very few lines

[20] Schneiderhölm and Ramdor, *Lehrbuch der Erzmikroskopie* (Berlin) 1931.

that do not correspond to the FeS-CrS type of structure were found in the X-ray diagrams of the inner layers of scale. The color of the FeS-CrS constituent changes from a distinct brassy-yellow in the outer layer to a light gray in the inner layer, due perhaps, to the higher proportion of chromium in the inner layers. The amount of pitting was much more pronounced in the inner layers and may be responsible for the dull appearance of these layers when examined visually. Fig. 21 shows that inclusions of the FeS-CrS constituent extended into the metal.

Discussion of Action of Oxygen and Hydrogen Sulphide on Iron-Chromium Alloys

The action of oxygen and of hydrogen sulphide upon iron-chromium alloys may now be considered in connection with the mechanism of scaling that has been developed.

Oxidation of Iron-Chromium Alloys—The characteristics of the various types of scale produced offer an explanation for the increase in the resistance of the iron-chromium alloys to oxidation as the chromium content of the alloys increases. The oxidation of the 12 per cent chromium alloy at temperatures of 1100 degrees Cent. and below resembles that of iron in that the two oxides Fe_2O_3 and Fe_3O_4 are formed, and consequently the transfer of oxygen inward and of metal outward is facilitated. In stating that there is a transfer of metal outward the authors wish to make clear that they are not inferring that there is necessarily a transfer of the metal in the metallic state, but only that there is a building up of the scale at the surface through a transfer of material outward through the scale as well as a continual formation of oxidized products at the scale-metal interface. As the chromium content of the scale increases the rate of scaling decreases and this effect is undoubtedly connected with the more stable character of the higher chromium scale. It is well known that chromium and aluminum, which form much more stable oxides than does iron, are also much more resistant to continued oxidation. This higher resistance to oxidation of the former metals is probably due to lower solubilities of the metals and of oxygen in the oxides together with the fact that oxides of a single composition are formed so that there is no possibility of oxidation-reduction reactions between oxides of different states of oxidation or between the metals and their oxides.

Some explanation must be found for the differences in composition of the scale. Preferential oxidation alone is evidently not sufficient, for chromium is more readily oxidized than iron until a definite layer of oxide is formed and the scale on the lower chromium alloy contained practically no chromium in the outer layer. It would seem that the differences in composition must be due to diffusion through the scale and the following explanation is offered. The first step of the oxidation process results in the formation of a surface layer of oxides of chromium and iron in which these metals are in the same proportions as in the original alloy. It is probable that chromic and ferric oxides are formed, since the pressure of oxygen in the furnace is greater than the dissociation pressure of either of these oxides; and furthermore, it is likely that these oxides are in the form of a solid solution since they have been shown to be completely miscible in the solid state.[20, 21, 22] Once this oxide layer is formed by direct oxidation then further oxidation must involve diffusion as well as chemical reactions. At the interface no oxide can be formed except by reaction with the scale or with dissolved oxygen which has diffused through the scale. If the maximum possible partial pressure of oxygen from these sources is less than that of the most stable oxide of iron then there can be no reaction between either the scale or the dissolved oxygen with the iron of the alloy. Under these circumstances only chromium will be oxidized and the reaction occurring at the metal-scale interface will be strictly a preferential oxidation of the chromium. If there is no appreciable solubility of iron in chromium oxide the amount of iron that diffuses to the scale-gas interface will be small and the scale will consist largely of chromic oxide. This is evidently the situation when alloys that contain more than about 25 per cent of chromium are oxidized at temperatures up to 1100 degrees Cent. It is apparent that once the chromium content of the initial scale is sufficient to prevent continued oxidation of iron then higher amounts of chromium cannot further increase the resistance of the alloys to oxidation.

Carrying this concept a step further it is seen that when the chromium content of the initial layer of scale is somewhat less it becomes possible for iron as well as chromium to be oxidized at the

[20] Wretblad, *Z. anorg. allgem. Chemie*, Vol. 189, 1930, p. 329-36.

[21] Passerini, *Gazz. Chim. Ital.*, Vol. 60, 1930, p. 544-58.

[22] Forestier and Chaudron, *Comptes Rendus*, Vol. 180, 1925, p. 1264-6.

scale-metal interface. The presence of iron in the scale increases the ability of the latter to transmit oxygen, possibly because of a series of oxidation-reduction reactions between different iron oxides. Some chromium may diffuse outward through the scale as metal or oxide, but evidently iron or iron oxide diffuses much more readily and the portion of the scale that builds up beyond the original surface of the specimen is largely iron oxide. This is shown by the chemical composition of the scale from the 12 per cent chromium alloy, the outer layer of which was mostly iron oxide while the inner layer contains a higher proportion of chromium than did the original alloy.

The foregoing concept of the scaling process explains the form of the composition-oxidation curves shown in Fig. 5. At the higher percentages of chromium the rate of oxidation is very low and apparently does not change appreciably as the chromium content increases. As the amount of chromium decreases the rate of oxidation suddenly begins to rise rapidly until the amount of chromium reaches a certain value below which this element has very little effect. It should be remembered that these curves are for a particular temperature and that at other temperatures these particular critical values of the chromium content may be different than at the temperatures for which these curves apply.

It was concluded from the proposed mechanism of oxidation that at extremely low oxygen pressures an alloy high in chromium would oxidize more than one containing less chromium. To check this conclusion the following tests were made. Specimens of alloys containing 12 and 28 per cent chromium were heated for 150 hours at 980 degrees Cent. in a furnace that was continuously evacuated during this time. A similar test was made with the specimens packed in chromic oxide and heated in the evacuated furnace. During both these tests the pressure within the furnace was of the order of 0.0005 millimeter of mercury. It was found that the loss of weight of the higher chromium alloy due to oxidation was more than ten times that of the other. When similar tests were carried out with the specimens packed in finely powdered ferric oxide it was found that, even though the evacuation was continuous as before, the pressure within the furnace was considerably greater and in this case the lower chromium alloy oxidized fully as much as the other and both oxidized more than in the other tests. The scale resulting from these tests was not analyzed but that formed on both alloys in the first tests was distinctly green in color, indicating that it was chiefly

chromium oxide, while that formed in contact with iron oxide was black in color and probably contained considerable iron oxide.

Action of Hydrogen Sulphide on Iron-Chromium Alloys—As a result of the action of hydrogen sulphide upon the alloys under discussion scale was produced that consisted principally of a single phase, and there is consequently little possibility of a series of reactions within the scale itself. The relatively high rates of scaling in hydrogen sulphide are very probably due to a high solubility of sulphur and of the metals in the scale. Both iron and sulphur are known to be quite soluble in FeS,[23] and it is probable that chromium is appreciably soluble in the FeS-CrS solid solution. Under these conditions sulphur will be readily transferred inward through the scale, and both iron and chromium as the dissolved metals or as sulphides comparatively low in sulphur, will be transferred outward. It must be concluded that the transfer of iron in this way is the more rapid, since the outer layer of scale was found to be largely FeS with excess sulphur. There must, however, also be some transfer of chromium in this manner since the second layer of scale which was outside the original surface of the specimen was found to contain a considerable proportion of this element. This slower rate of diffusion of chromium may be the reason for the slightly greater resistance of the higher chromium alloy to attack by hydrogen sulphide.

Effect of Temperature and Time—It has already been shown that the temperature coefficients of reaction that were found are consistent with the hypothesis that rates of diffusion determine the rate of scaling under the conditions of this work. There are not enough data available to explain the difference in the forms of the temperature-scaling curves for scaling in oxygen and in hydrogen sulphide.

The relation of time and the amount of diffusion of a material is expressed by the relationship $dW = -D\frac{dc}{dx}dt$, that has already been given. If it be assumed that D remains constant, that x, the thickness of the layer through which diffusion takes place, is proportional to W, the amount of substance which has diffused at a given time, and that the concentration gradient, $\frac{dc}{dx}$, of the diffusing substance is inversely proportional to the thickness of the layer through which diffusion takes place, then the foregoing equation leads to the

[23] Benedicts and Löfquist, "Non-metallic Inclusions in Iron and Steel," 1931, p. 14.

relationship $W^2 = kt$, where k is a constant under a given set of conditions. The derivation of this expression has already been given in the literature[14, 24] and will not be repeated here. The relation of time to amount of scaling was found in the present work to follow equations of the form $W^n = kt$, where n was 2 in the case of the oxidation of a low carbon steel containing no chromium and was less than 2 in every other case. This means, of course, that in the latter cases the amount of scaling was more nearly proportional to the time than the ideal integrated form of the diffusion law requires. This does not necessarily mean that diffusion is not the determining factor, but may mean that the assumptions upon which the integration is based are not strictly true. Physical changes in the scale such as fissuring or changes in chemical composition during the process of scaling would change the value of D, and the latter factor might also change the relation of the concentration gradient to the thickness of the scale.

It is evident that there are several points in connection with the mechanism of scaling of these alloys on which more information is desirable, but the hypothesis that has been offered is not inconsistent with any of the results observed in the present work and seems to offer a working basis for explaining the behavior of iron-chromium alloys in atmospheres of the type studied.

Summary and Conclusions

The most important results of this investigation may be briefly summarized as follows.

1. The resistance of iron-chromium alloys to oxidation at a given temperature increases relatively slowly at first and then very rapidly as the chromium content of the alloys increases. A chromium content is finally reached beyond which further additions of this element have little additional effect.

2. The scaling of these alloys in hydrogen sulphide at temperatures of from 760 to 1090 degrees Cent. (1400 to 2000 degrees Fahr.) is much greater and the effect of increasing amounts of chromium is much less than in oxygen under similar conditions.

3. The rate of scaling in both oxygen and hydrogen sulphide

[14] Pilling and Bedworth, Loc. cit.

[24] Dunn, *Proceedings*, Royal Society, London, Vol. 111A, 1926, p. 210-19.

decreased as the time increased and, except in the case of oxidation of a 28 per cent chromium alloy, increased rapidly as the temperature increased up to 1090 degrees Cent. (2000 degrees Fahr.).

4. The increased resistance to oxidation of the higher chromium alloys was found to be accompanied by a great increase in the proportion of chromium in the scale.

5. Observations of the character of the scale and a consideration of the published results of another investigation support the hypothesis that there is a diffusion of both the reacting gas or of higher products of reaction inward and of the metal or of lower products of reaction outward through the scale.

6. On the basis of such a hypothesis it is possible to explain the effect of chromium content on the resistance to oxidation and to attack by hydrogen sulphide, and to account for the compositions of the various types of scale. The effects of temperature and of time are not inconsistent with this hypothesis.

Acknowledgments

The authors desire to express their appreciation to Dr. L. Thomassen for his assistance with the X-ray work and his suggestions during the course of the investigation, to L. A. Delp who made most of the chemical determinations, and to all others who have contributed in any way to this investigation.

DISCUSSION

Written Discussion: By Dr. L. B. Pfeil, research laboratory, The Mond Nickel Co. Ltd., Birmingham, England.

Dr. Pfeil wrote that he had read Messrs. Rickett and Wood's paper with special interest, since he had himself carried out researches on the fundamental aspects of the scaling of steels. He was gratified to find that the authors' work on iron-chromium alloys tended to support the hypothesis that the scaling of ferrous alloys involved the counter-current diffusion of oxygen inwards and iron outwards through the scale. The authors' results on the sulphur attack of iron-chromium alloys established with reasonable certainty that the mechanism involved was also of the counter-current type, sulphur diffusing inwards and iron, and to a lesser extent chromium, outwards.

In iron-chromium alloys in particular he considered that diffusion within the metallic core was slower than the conversion of metal to oxide or sulphide, thus making preferential attack a factor of minor importance. The composition of the various scale layers in ferrous alloys was determined principally by the rate of outward diffusion of the various metallic atoms, and in his view the

rate of diffusion of chromium in oxide scale was extremely small. During the oxidation of iron-chromium alloys the chromium atoms remained substantially stationary, while the diffusion of iron outwards led to an enrichment of chromium in the depth of the scale. In this connection he was inclined to suspect some error in the chromium determinations recorded for the 20 per cent chromium alloy in Table III. The figures indicated that, whereas in the inner scale layer produced at 1090 degrees Cent. the chromium to iron ratio was about the same as in the original steel, the ratio in the outer layer was much less than in the original steel. This suggested that the unoxidized steel core was enriched in chromium, an effect which he had never been able to demonstrate (the figure of 5.32 per cent given for manganese in Table III is perhaps a printing error).

To produce a steel of high heat resisting capacity it seems necessary to adjust the composition so that a scale is produced through which iron cannot readily diffuse. This may be done by raising the chromium content, which the authors' work shows results in the formation of a chromium-rich iron-chromium-oxygen solid solution. When, from the point of view of mechanical properties, or from other reasons, an iron-chromium alloy of high-chromium content is objectionable, another method is available for producing a scale through which iron cannot readily diffuse, viz., the replacement of part of the iron in the iron-chromium alloy by nickel. Such a replacement raises the iron to chromium ratio, but at the same time leads to the formation within the scale of nickel particles or filaments, which assist in blocking the diffusion path.

In Fig. 14 Messrs. Rickett and Wood illustrate the constituents in the inner layer of the scale produced on the 12 per cent chromium alloy in oxygen at 980 degrees Cent. Of the constituents shown in the photograph, three can with reasonable certainty be attributed to:

(a) metallic nickel—the small white particles,
(b) ferrous silicate—the dark grey constituent,
(c) the iron-chromium-oxygen solid solution—the light grey groundmass.

The remaining constituent may perhaps be an excess of ferrous oxide phase or an excess of magnetite which has separated from the solid solution during cooling. The analytical results given in Table I do not include, in the case of the 12 per cent chromium alloy, a figure for silicon and for nickel, but it seems probable that small quantities of both these elements were present. A small amount of silicon can, of course, result in the production of a considerable volume of ferrous silicate in the inner scale layer, while in his (Dr. Pfeil's) experience as little as 0.1 per cent nickel in steel frequently gives rise to clearly visible particles of metallic nickel in the inner scale layer.

With respect to the formation of layers in scale deposits, he would be interested to learn Messrs. Rickett and Wood's views on why there should be a plane of demarcation in a scale deposit corresponding with the original surface of the steel. In some alloy steels this was understandable on the basis that certain alloying elements remained in that portion of the scale which lay within the original boundaries of the specimen, whereas the remainder of the scale

consisted essentially of iron oxide. In the case of pure iron, however, the line of demarcation was equally well defined and no completely satisfying explanation of its cause was yet known to him.

Finally he wished to ask the authors whether they had any explanation to offer for the existence of three scale layers within the original boundaries of the 11 per cent chromium specimen scaled in sulphuretted hydrogen. In the absence of the authors' assurance that the temperature was held constant within ± 7 degrees Cent. he would have been inclined to attribute the formation of these sub-layers to temperature variations or gas velocity variations during the experiments.

Written Discussion: By Norman B. Pilling, manager, research laboratory, International Nickel Co., Bayonne, N. J.

It is a pleasure indeed to welcome this thoughtful contribution. Although the application of heat resisting metals to engineering use is far advanced, it must be admitted with some reluctance that our understanding of the real reasons they have proved to be so useful to us are still rather hazy; it is curious to reflect how few have been the efforts to analyze the principles underlying this important branch of metallurgy. This paper is a very acceptable step in the process of catching up with ourselves.

The authors would probably not intend to have their data taken as a full and complete guide to the action of sulphur on iron-chromium alloys. Fig. 7 is quite suggestive regarding the connection between chromium content and rate of attack under highly reducing conditions, but there are other factors of importance which lie outside of the scope of their study. A characteristic of some importance is the melting point of the sulphide scale; this seems to increase with chromium content and does have some bearing on the maximum temperature to which the materials are useful. The chromium-rich inner sulphide layer has been noted before and the importance of its properties in defining resistance to sulphidizing attack is certainly considerable. Perhaps the most common occurrence of sulphur at high temperature is with other oxidizing gases, and its behavior with chromium alloys under these conditions departs very considerably from that shown by hydrogen sulphide.

I would be inclined to think that the paper is most valuable in its effort to develop the physical mechanism of scaling as applied to the complex alloys. The precision with which the oxidation of a number of simple metals has been found to conform to the parabolic law, when sufficient care is taken to eliminate disturbing factors, makes it likely that the 1.5 power found with the alloys has some deeply important significance; an integration which would develop this, without doing violence to the requirements of diffusion, would go far toward disclosing the dominant factors which are concerned. A similar effect was noted by Pilling and Bedworth (*Journal of Industrial and Engineering Chemistry*, 1925) in the oxidation of copper-nickel alloys; in that case also the richer alloys dropped to a power which was close to 1.5.

It might perhaps not be out of place to suggest, since concentration gradients of the reactive atoms within the scale enter so completely into the present-day conceptions of high temperature corrosion, that an experimental study in which these gradients are under control should be quite revealing. While such control of metal-atom gradients is not directly possible, those of oxygen or

other reactant having an external source can be made so, through operations at suitably low absolute pressures and fortunately the technique is not difficult. The table below gives data which may be of some use, showing changes in oxidation rate of iron at 800 degrees Cent. as the absolute oxygen pressure

Effect of Oxygen Concentration on Oxidation Rate of Armco Iron at 800 Degrees Cent.

No.	Absolute Oxygen Pressure Millimeters of Mercury	Increase in Weight Grams Per Square Centimeter in First Hour
1	.075	0.00018
2	.18	0.0060
3	1.14	0.011
4	1.14	0.011
5	19.3	0.012
6	18.5	0.010
7	20.5	0.011
8	50.0	0.011
9	150.	0.012
10	149.	0.012
11	730.	0.015
12	730.	0.015

is changed from 730 millimeters down to about 0.08 millimeters of mercury. It indicates that until the pressure is reduced to about 0.20 millimeters the oxidation rate is reduced but little, but below it the rate diminished very rapidly indeed. Presumably this external pressure is that which is in equilibrium with oxygen at the point of maximum solubility in the scale, and lower pressures have an immediate effect upon the oxygen gradient.

High temperature metals still require much necessary work dealing with creep strength and other properties of immediate utility, but in the maze of these complicated investigations the importance of such studies as this which Professor Wood has undertaken should not be overlooked; we shall be fortunate if he is encouraged to continue.

H. W. McQuaid: I can say that in chromium iron carburizing boxes I have noticed that the difference in the life of the box is indicated by the color of the scale formed (particularly true in the nickel-chromium boxes). If you get a typical oxide scale they are relatively short lived, and unfortunately, that is the common scale you get. We have had quite a few boxes which turn a chocolate red, and I have known them to run as high as 7000, 8000, and 10,000 hours, as compared to the usual average of 2000 and 3000 hours, without showing any oxidation. We went to a lot of trouble to find out why the one kind of scale was protective coating and the other was not, but we were not successful, probably because we did not go into it sufficiently far, and most probably through ignorance as to how to do it correctly.

W. E. Jominy: This paper is so complete, there seem hardly any questions to ask. There are many difficulties involved in these scaling tests and I think the authors have done a mighty fine piece of work. The question that arises in my mind is whether there were differences in the form of oxides with different temperatures, and whether there might be differences in the form of sulphides at different temperatures, and whether any attempt was made to de-

termine the elements other than manganese and chromium and iron. I have often wondered how those other elements oxidized.

Authors' Closure

The authors wish to express their appreciation to those who, by their discussion, have contributed so much to the value of this paper.

Mr. McQuaid reports a very interesting observation regarding the relation of the type of scale produced to the life of carburizing boxes in service. The study of gaseous attack of commercial heat resistant alloys is a complex problem and the work of the present authors represents only a beginning in its solution. Mr. McQuaid's remarks indicate the real need that exists for continued work along this line.

Mr. Jominy asks about the influence of temperature upon the form of oxides and of sulphides and whether any attempt was made to determine elements other than iron, chromium and manganese in the scale. No determinations of these other elements were made, and very little information was obtained regarding the type of oxides and sulphides formed at different temperatures. Both of these factors are important, but it was necessary to restrict the extent of the present investigation. In previous work the authors have found that elements such as silicon, nickel, and tungsten may have a very considerable influence on the type of scale produced.

Dr. Pilling has evidently had considerable experience along the lines of this investigation, and it is to be hoped that he and the others who are obtaining fundamental information in this field will soon be able to present their findings to the public. The authors agree fully with Dr. Pilling that when present with oxidizing gases the behavior of sulphur may be entirely different than under the conditions of this work. With some alloys the rate of attack is greatly reduced in the presence of oxidizing gases; in the case of certain other alloys it may be considerably increased under such circumstances.

We do not believe that the departure of the scaling curves for the iron-chromium alloys from the parabolic law is at all surprising in view of the possibiilities that exist for changes in the physical and chemical characteristics of the scale as the thickness of scale increases. We doubt, however, that any simple mathematical relationship will be found to express these changes.

Data of the type given by Dr. Pilling in the table are of interest in determining the maximum solubility of oxygen in the scale. The fact that the oxygen pressure may influence both the type and amount of scale formed on iron-chromium alloys has already been pointed out by the authors in this paper.

The remarks of Dr. Pfeil like those of Dr. Pilling are particularly valued because they come from one who has contributed much to the fundamental knowledge of scaling processes. Dr. Pfeil's interpretation of the authors' Fig. 14 is appreciated.

The authors are substantially in accord with the interpretation of the scaling process offered by Dr. Pfeil. They do not agree, however, that the chromium determinations recorded for the 20 per cent chromium alloy in Table III are appreciably in error. It is true that the outer layer formed at 1090 degrees Cent. was considerably depleted in chromium, and that the inner layer

was enriched to a much lesser extent so far as percentage is concerned. However, this inner layer was considerably thicker than the outer layer. We have made a few determinations of chromium in the outer layers of metal after oxidation, and like Dr. Pfeil, have never found any evidence that the alloy was enriched in chromium. The figure of 5.32 per cent given for manganese in Table III is not a printing error. The amount of scale available for analysis was so extremely small in the case of this alloy that no great accuracy is claimed for the analytical results. However, it was very definitely established that an unexpectedly high proportion of manganese was present, which in view of the amount in the original alloy would indicate that the diffusion of this element was much more rapid than that of iron.

In conclusion Dr. Pfeil raises some questions upon which both he and the present authors would like further enlightenment. We have nothing but conjecture to offer by way of explanation of the presence of a surface of demarcation at the original boundary of the alloy. We have some evidence that the scale built up outside the original surface is more continuous, that is, has less voids than that formed inside the original boundary. However, we do not know that this is universally true, or if it is that it is responsible for the surface of demarcation. Also, we know of no reason why there should be three layers of scale inside the original surface in the case of the specimens heated in hydrogen sulphide. There is no sharp change in the type of micro-constituents from layer to layer that could be observed. We do not believe that the presence of three layers could be due to variations of temperature or of gas velocity, since these layers were observed in a large number of specimens run independently and for different lengths of time. It is not conceivable that these variations would be at all similar in all cases.

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